Electronic Supplementary Information

1. General Experimental Procedures

Commercially available reagents were used as received from suppliers. Solvents were laboratory grade and dried using an appropriate drying agent when required. Reactions requiring anhydrous conditions were carried out under an atmosphere of dry argon using Schlenk-line techniques. Where appropriate, solvents were degassed using the freeze-thaw cycle method.

Thin-layer chromatography was carried out on silica plates (Merck 5554) or neutral alumina plates (Merck Art 5550) and visualised under UV (254/365 nm) irradiation or by staining with iodine. Preparative column chromatography was carried out using silica (Merck Silica Gel 60, 230400 mesh) or neutral alumina (Merck Aluminium Oxide 90, activity II-III, 70230 mesh), pre-soaked in ethyl acetate.

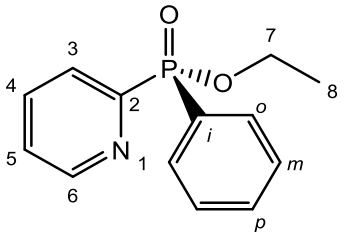
pH measurements were carried out at 295 K using a Thermo Scientific Orion Star A111 pH meter with a Sigma-Aldrich micro-pH combination electrode. Calibration was performed using commercially available buffer solutions at pH = 4.0 ±0.02, pH = 7.00 ±0.02 and pH = 10.00 ±0.02.

NMR spectra (^{1}H, ^{13}C, ^{31}P) were recorded on a Varian VXR-400 spectrometer (^{1}H at 399.97 MHz, ^{13}C at 100.57 MHz, ^{31}P at 161.91 MHz) or a Varian VNMRS-700 spectrometer (^{1}H at 699.73 MHz, ^{13}C at 175.95 MHz). Spectra were recorded at 295 K in commercially available deuterated solvents and referenced internally to the residual solvent proton resonances.

Both electrospray and high resolution mass spectrometry were performed on a Thermo-Finnigan LTQ FT system using methanol as the carrier solvent.

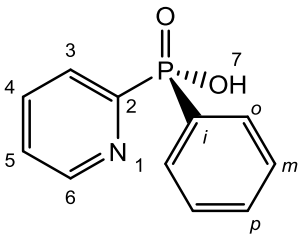
2. Synthetic Procedures

Ethyl phenyl(2-pyridyl)phosphinate



2-Bromopyridine (0.60 mL, 6.33 mmol), ethyl phenylphosphinate (1.15 mL, 7.610 mmol) and triethylamine (3.61 mL, 25.8 mmol) were added to anhydrous degassed toluene (11 mL). [1,1'-Bis(diphenylphosphino)-ferrocene] dichloropalladium(II) (0.072 g, 0.098 mmol) was added and the mixture was degassed, heated to reflux and stirred for 16 h under nitrogen. The solution was diluted with CH_2Cl_2 (20 mL), washed with HCl (1 M, 2 x 25 mL) and water (3 x 20 mL), dried over K_2CO_3, filtered and the solvent removed under reduced pressure to give a clear yellow oil. Purifcation by column chromatography on silica (CH_2Cl_2 : 2% MeOH) gave the title compound as a yellow oil (0.82 g, 53%): $\boldsymbol{\delta_H}$ (400 MHz; MeOD) 8.76 (1H, ddd, $^3J_{HH}$ 4.8 Hz $^4J_{HP}$ 1.0 Hz $^4J_{HH}$ 1.2 Hz, H^6), 8.11 (1H, tdd, $^3J_{HH}$ 6.5 Hz $^4J_{HP}$ 5.9 Hz $^4J_{HH}$ 1.2 Hz, H^4), 8.00 (1H, ddd, $^3J_{HP}$ 12.4 Hz $^3J_{HH}$ 4.8 Hz $^4J_{HH}$ 1.6 Hz, H^3), 7.95-7.90 (2H, m, H^o), 7.67-7.62 (1H, m, H^5), 7.60-7.52 (1H, m, H^p), 7.60-7.52 (2H, m, H^m), 4.15 (2H, qd, $^3J_{HH}$ 6.5 Hz $^3J_{HP}$ 4.0 Hz, H^7), 1.40 (3H, t, $^3J_{HH}$ 6.5 Hz, H^8); $\boldsymbol{\delta_C}$ (100 MHz, MeOD) 150.4 (d, $^3J_{CP}$ 20.3 Hz, C^6), 146.6 (d, $^1J_{CP}$ 227 Hz, C^2), 135.8 (d, $^2J_{CP}$ 174 Hz, C^3), 132.7 (d, $^4J_{CP}$ 2.8 Hz, C^5), 131.8 (d, $^3J_{CP}$ 10.1 Hz, C^4), 128.4 (d, $^3J_{CP}$ 13.3 Hz, C^m), 127.9 (C^o), 126.3 (d, $^4J_{CP}$ 3.2 Hz, C^p), 80.9 (d, $^1J_{CP}$ 275 Hz, C^i), 62.0 (C^7), 15.3 (C^8); $\boldsymbol{\delta_P}$ (162 MHz, MeOD) 27.0; IR (neat) 3057 (C–H), 1218 (P=O), 1022 (P–O) cm^{-1}; m/z (ESI+) 248.0840 $[M + H]^+$ ($C_{13}H_{15}NO_2P$ requires 248.0843); R_f = 0.46 (silica, CH_2Cl_2 : 4% MeOH).

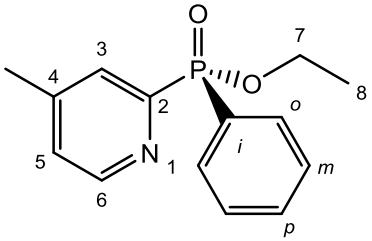
Phenyl(2-pyridyl)phosphinic acid



Ethyl phenyl(2-pyridyl)phosphinate (0.82 g, 3.32 mmol), was dissolved in HCl (6 M, 1 mL) and stirred at 100 °C for 16 h. The solvent was lyophilised under high vacuum to give the title compound as a pale yellow solid (quantitative); $\boldsymbol{\delta_H}$ (400 MHz; MeOD) 8.97 (1H, d, $^3J_{HH}$ 6.0 Hz, H^6), 8.73 (1H, tdd, $^3J_{HH}$ 7.8 Hz $^4J_{HP}$ 1.2 Hz $^4J_{HH}$ 0.8 Hz, H^4), 8.45 (1H, dd, $^3J_{HH}$ 7.8 Hz $^3J_{HP}$ 6.0 Hz, H^3), 8.22 (1H, t, $^3J_{HH}$ 6.0 Hz, H^5), 7.99 (2H, dd, $^3J_{HP}$ 7.0 Hz $^3J_{HH}$ 6.0 Hz, H^o), 7.69-7.65 (1H, m, H^p), 7.61-7.56 (2H, m, H^m), 5.51 (1H, br s,

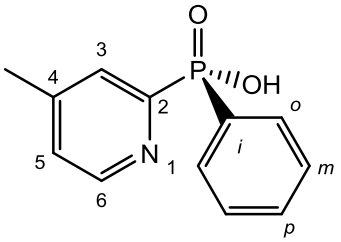
H^{7}); **δ_C** (100 MHz, MeOD) 150.9 (d, $^{1}J_{CP}$ 129 Hz, C^{2}), 146.9 (C^{3}), 143.4 (d, $^{4}J_{CP}$ 6.7 Hz, C^{5}), 133.3 (d, $^{4}J_{CP}$ 2.8 Hz, C^{p}), 131.8 (d, $^{3}J_{CP}$ 10.7 Hz, C^{4}), 130.7 (d, $^{1}J_{CP}$ 147 Hz, C^{i}), 130.4 (d, $^{2}J_{CP}$ 11.4 Hz, C^{o}), 128.9 (d, $^{3}J_{CP}$ 13.8 Hz, C^{6}), 128.1 (d, $^{3}J_{CP}$ 14.8 Hz, C^{m}); **δ_P** (162 MHz, MeOD) 13.1; m/z (ESI+) 220.0544 $[M + H]^+$ ($C_{11}H_{11}NO_2P$ requires 220.0527).

Ethyl phenyl(4-methylpyridin-2-yl) phosphinate



Ethyl phenylphosphinate (0.50 g, 2.94 mmol), 2-bromo-4 methylpyridine (0.32 mL, 2.94 mmol) and triethylamine (0.40 mL, 2.94 mmol) were dissolved in toluene (5 mL) and the solution degassed using argon. $PdCl_2$(dppf) (0.10 g, 0.15 mmol, 3 mol%) was added and the resulting mixture refluxed for 16 h at 120 °C under argon. The solution was diluted using CH_2Cl_2 (30 mL), washed with HCl (1 M, 2 x 50 mL) followed by water (2 x 50 mL), dried over K_2CO_3, filtered and the solvent removed under reduced pressure to give a dark brown residue. The crude product was purified by column chromatography on silica (CH_2Cl_2 : 0.5% MeOH) to give the title compound as a yellow oil (0.27 g, 34%): **δ_H** ($CDCl_3$) 8.60 (1H, d, $^{3}J_{HH}$ 7.0 Hz, H^{6}), 7.98-7.95 (1H, m, H^{5}), 7.98-7.95 (2H, m, H^{o}), 7.50 (1H, tq, $^{3}J_{HH}$ 7.5 Hz $^{4}J_{H\text{-}H}$ 2.7 Hz, H^{p}), 7.43 (2H, tdd, $^{3}J_{HH}$ 7.4 Hz $^{4}J_{HH}$ 3.6 Hz $^{5}J_{HH}$ 1.4 Hz, H^{m}), 7.16 (1H, d, $^{4}J_{HH}$ 4.9 Hz, H^{3}), 4.13 (1H, dqd, $^{3}J_{HP}$ 20 Hz $^{2}J_{HH}$ -12 Hz $^{3}J_{HH}$ 7.0 Hz, H^{7}), 4.10 (1H, dqd, $^{3}J_{HP}$ 20 Hz $^{2}J_{HH}$ -12 Hz $^{3}J_{HH}$ 7.0, H$^{7'}$), 2.38 (3H, s, H$^{4\text{-}Me}$), 1.35 (3H, t, $^{3}J_{HH}$ 7.0 Hz, H^{8}); **δ_C** ($CDCl_3$) 154.2 (d, $^{1}J_{C\text{-}P}$ 166 Hz, C^{2}), 150.3 (d, $^{3}J_{C\text{-}P}$ 21.1 Hz, C^{6}), 147.5 (d, $^{3}J_{C\text{-}P}$ 10.4 Hz, C^{4}), 132.3 (d, $^{4}J_{C\text{-}P}$ 2.8 Hz, C^{p}), 132.2 (2C, d, $^{2}J_{CP}$ 9.7 Hz, C^{o}), 130.3 (d, $^{1}J_{CP}$ 137 Hz, C^{i}), 129.2 (d, $^{4}J_{CP}$ 23 Hz, C^{5}), 128.3 (2C, d, $^{3}J_{CP}$ 13 Hz, C^{m}), 126.4 (d, $^{2}J_{CP}$ 3.3 Hz C^{3}), 61.6 (d, $^{2}J_{CP}$ 6.1 Hz, C^{7}), 24.0 (d, $^{4}J_{CP}$ 6.1 Hz, C$^{4\text{-}Me}$), 16.5 (d, $^{3}J_{CP}$ 6.2 Hz, C^{8}); **δ_P** ($CDCl_3$) 25.9; *m/z* (HRMS^{+}) 262.1000 $[M + H]^+$ ($C_{14}H_{17}NO_2P$ requires 262.0997).

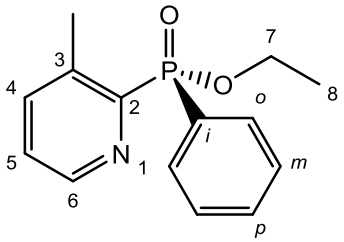
Phenyl (4-methylpyridin-2-yl) phosphinic acid



Ethyl phenyl (4-methylpyridin-3-yl)phosphinate (0.27 g, 1.1 mmol) was dissolved in a solution of HCl (6 M, 2.0 mL) and the mixture was stirred at 90 °C for 16 h. The solvent was removed under high vacuum and washed with dry methanol (2 x 3 mL).Methanol was removed under reduced pressure and the residue dried under high vacuum to give the title compound as a brown oil (quantitative): **δ_H** (CD_3OD) 9.15 (1H, br m, H^{6}), 8.06 (1H, br m, H^{5}), 8.00 (2H, br m, H^{o}), 7.68 (1H, br m, H^{p}), 7.45 (1H, br m, H^{3}), 7.38 (2H, br m, H^{m}), 2.58 (3H, s, H$^{4\text{-}Me}$); **δ_C** (CD_3OD) 159.3 (d, $^{1}J_{CP}$ 3 Hz, C^{2}), 148.5 (s, C^{4}), 142.8

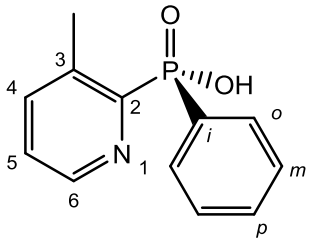
(s, C^6), 132.8 (s, C^3), 132.3 (2C, s, C^o), 131.1 (s, C^5), 129.7 (s, C^i), 128.9 (2C, s, C^m), 128.8 (s, C^p), 22.5 (s, $C^{4\text{-Me}}$); δ_P (CD_3OD) 11.1; *m/z* (HRMS$^+$) 234.0684 $[M + H]^+$ ($C_{12}H_{13}NO_2P$ requires 234.0682).

Ethyl phenyl(3-methylpyridin-2-yl)phosphinate



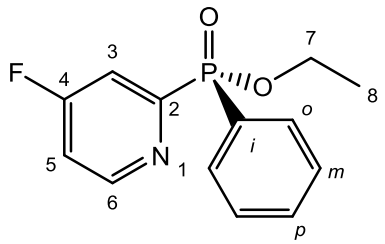
Ethyl phenylphosphinate (0.44 mL, 2.94 mmol), 2-bromo-3-methylpyridine (0.32 mL, 2.94 mmol) and triethylamine (0.41 mL, 2.94 mmol) were dissolved in anhydrous toluene (5 mL). After the addition of $PdCl_2$(dppf) (0.064 g, 0.09 mmol, 3 mol%), the solution was degassed for 2 h using argon and then heated to 120 °C for a further 16 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2 : 2% MeOH) to give the title compound as a yellow oil (0.62 g, 80%): δ_H ($CDCl_3$) 8.57 (1H, dd, $^3J_{HH}$ 8.0 Hz $^4J_{HH}$ 0.9 Hz, H^6), 7.92 (2H, dq, $^3J_{HH}$ 11 Hz $^4J_{HH}$ 5.0 Hz, H^o), 7.57-7.52 (1H, m, H^5), 7.57-7.52 (1H, m, H^4), 7.47 (2H, tdd, $^3J_{HH}$ 11 Hz $^4J_{H\text{-}H}$ 5.0 Hz $^5J_{HH}$ 1.3 Hz, H^m), 7.27 (1H, td, $^3J_{HH}$ 11 Hz $^4J_{HH}$ 5.0 Hz, H^p), 4.23 (2H, m, $^2J_{HH}$ -12 Hz $^3J_{HH}$ 9.0 Hz, H^7), 2.67 (3H, s, $H^{3\text{-Me}}$), 1.41 (3H, t, $^3J_{HH}$ 9.0 Hz H^8); δ_C ($CDCl_3$) 152.4 (d, $^1J_{CP}$ 293 Hz, C^2), 147.0 (d, $^3J_{CP}$ 35.7 Hz, C^6), 139.2 (d, $^2J_{CP}$ 43.0 Hz, C^3), 138.9 (d, $^3J_{CP}$ 18.0 Hz, C^4), 132.2 (s, C^5), 132.1 (s, C^p), 131.2 (d, $^1J_{CP}$ 237.7 Hz, C^i), 128.3 (2C, d, $^2J_{CP}$ 22.8 Hz, C^o), 125.3 (2C, d, $^3J_{CP}$ 6.0 Hz, C^m), 61.6 (d, $^2J_{CP}$ 10.8 Hz, C^7), 19.5 (s, $C^{3\text{-Me}}$), 16.5 (d, $^3J_{CP}$ 10.7 Hz, C^8); δ_P ($CDCl_3$) 28.9; *m/z* (HRMS$^+$) 262.0998 $[M + H]^+$.

Phenyl (3-methylpyridin-2-yl)phosphinic acid



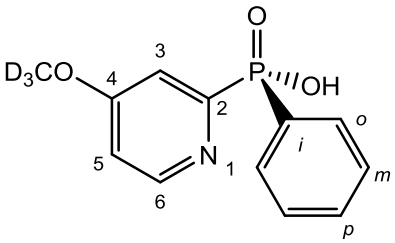
Ethyl phenyl(3-methylpyridin-3-yl)phosphinate (0.62 g, 2.36 mmol) was dissolved in a solution of HCl (6 M, 2.0 mL) and the mixture was stirred at 90 °C for 16 h. The solvent was removed under high vacuum and washed with dry methanol (2 x 3 mL).Methanol was removed under reduced pressure and the residue dried under high vacuum to give the title compound as a brown oil (quantitative): δ_H (CD_3OD) 8.83 (1H, d, $^3J_{HH}$ 7.5 Hz, H^6), 8.47 (1H, dd, $^3J_{HH}$ 7.5 Hz $^4J_{HH}$ 4.2 Hz, H^4), 8.11 (1H, t, $^3J_{HH}$ 7.5 Hz, H^5), 7.86 (2H, ddd, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 1.3 Hz $^5J_{HH}$ 0.7, H^o), 7.64 (1H, td, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 1.3 Hz, H^p), 7.54 (2H, td, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 1.3 Hz, H^m), 2.53 (3H, s, $H^{3\text{-Me}}$); δ_C (CD_3OD) 149.0 (d, $^3J_{CP}$ 7.4 Hz, C^4), 147.5 (d, $^1J_{CP}$ 125 Hz, C^2), 142.2 (d, $^2J_{CP}$ 12 Hz, C^3), 140.3 (d, $^3J_{CP}$ 6.0 Hz, C^6), 133.6 (d, $^2J_{CP}$ 11 Hz, C^o), 133.1 (d, $^3J_{CP}$ 2.9 Hz, C^m), 130.8 (d, $^1J_{CP}$ 147 Hz, C^i), 128.8 (s, C^5), 128.07 (s, C^p), 17.7 (d, $^3J_{CP}$ 1.6 Hz, $C^{3\text{-Me}}$); δ_P (CD_3OD) 12.6; *m/z* (HRMS$^+$) 234.0688 $[M + H]^+$ ($C_{12}H_{13}NO_2P$ requires 234.0684).

Phenyl (4-fluoropyridin-2-yl) phosphinate, L1



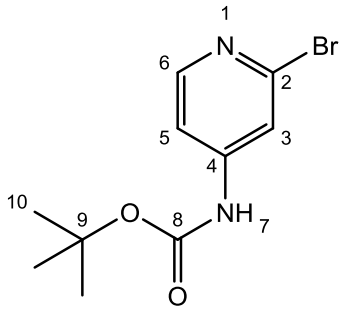
Ethyl phenylphosphinate (0.41 mL, 2.74 mmol), 2-bromo-4-fluoropyridine (0.48 g, 2.74 mmol) and triethylamine (0.38 mL, 2.74 mmol) were dissolved in toluene (5 mL) and the mixture was stirred at room temperature for 2 h, while argon gas was bubbled through solution. $PdCl_2$(dppf) (0.06 g, 0.082 mmol, 3 mol%) was added and the solution was heated to 120 °C and stirred for a further 16 h. Toluene was removed under reduced pressure and the crude oil dissolved into CH_2Cl_2 (30 mL), washed with HCl (0.1 M, 1 x 30 mL) and water (2 x 30 mL) and the organic layer was dried using K_2CO_3, filtered and the solvent removed under reduced pressure. The crude residue was purified by column chromatography on silica (CH_2Cl_2 : 1.8% MeOH) to give the title compound as a pale yellow oil (0.13 g, 17%): $\boldsymbol{\delta_H}$ ($CDCl_3$) 8.73 (1H, dd, $^3J_{HH}$ 7.7 Hz $^4J_{HH}$ 0.9 Hz , H^6), 7.97 (2H, td, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 1.9 Hz, H^o), 7.87 (1H, dd, $^3J_{HH}$ 7.7 Hz $^4J_{HH}$ 2.5 Hz, H^5), 7.54 (1H, td, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 1.5 Hz, H^p), 7.47 (2H, td, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 3.0 Hz, H^m), 7.09 (1H, td, $^4J_{HH}$ 2.5 Hz $^3J_{HF}$ 6.0 Hz, H^3), 4.1 (2H, septet, $^3J_{HH}$ 7.1 Hz, H^7), 1.38 (3H, t, $^3J_{HH}$ 7.1 Hz, H^8); $\boldsymbol{\delta_C}$ ($CDCl_3$) 168.5 (dd, $^1J_{CF}$ 265 Hz $^3J_{CP}$ 16 Hz, C^4), 158.4 (dd, $^1J_{CP}$ 167 Hz $^3J_{CF}$ 4.5 Hz, C^2), 153.2 (dd, $^3J_{CF}$ 23 Hz $^3J_{CP}$ 6.1 Hz, C^2), 132.6 (d, $^4J_{CP}$ 2.7 Hz, C^p), 132.3 (2C, d, $^2J_{CP}$ 9.8 Hz, C^o), 129.5 (d, $^1J_{CP}$ 140 Hz, C^i), 128.5 (2C, d, $^3J_{CP}$ 13 Hz, C^m), 116.5 (dd, $^2J_{CF}$ 23 Hz $^4J_{CP}$ 17 Hz, C^5), 113.3 (dd, $^2J_{CF}$ 16 Hz $^2J_{CP}$ 2.5 Hz, C^3), 61.9 (d, $^2J_{CP}$ 6.2 Hz, C^7), 16.5 (d, $^2J_{CP}$ 6.2 Hz, C^8); $\boldsymbol{\delta_P}$ ($CDCl_3$) 24.2 (d, $^4J_{FP}$ 11 Hz); $\boldsymbol{\delta_F}$ ($CDCl_3$) -100.42 (dt, $^3J_{FP}$ 11 Hz); *m/z* (HRMS$^+$) 266.0746 $[M + H]^+$ ($C_{13}H_{13}FNO_2P$ requires 266.0746).

Phenyl (4-3d-methoxypyridin-2-yl)phosphinic acid



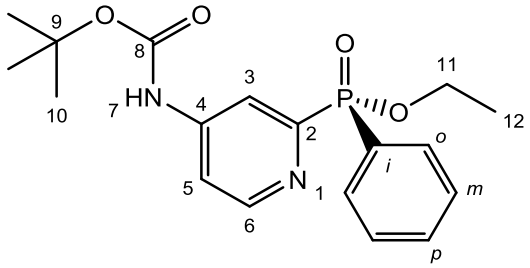
NaOH (0.042 g, 1.05 mmol) was dissolved in D_2O (1.5 mL) and added to a solution of phenyl(3-fluoropyridin-5-yl)phosphinate, **L1**, (0.14 g, 0.52 mmol) in MeOD (3 mL). The solution was stirred under argon at 30 °C, monitored directly by ^{1}H NMR. The solvent was lyophilised to yield the title compound as a powdery white solid (quantitative): $\boldsymbol{\delta_H}$ (CD_3OD) 8.49 (1H, dd, $^3J_{HH}$ 6.7 Hz $^5J_{HH}$ 1.6 Hz, H^6), 7.91 (2H, dd, $^3J_{HH}$ 7.5 Hz $^4J_{HH}$ 5.0 Hz, H^o), 7.63 (1H, t, $^3J_{HH}$ 7.5 Hz, H^p), 7.56-7.52 (2H, m, H^m), 7.56-7.52 (1H, m, H^3), 7.28 (1H, dd, $^3J_{HH}$ 6.7 Hz $^4J_{HH}$ 2.2 Hz, H^5); $\boldsymbol{\delta_C}$ (CD_3OD) 172.2 (d, $^3J_{CP}$ 11 Hz, C^4), 152.5 (d, $^1J_{CP}$ 128 Hz, C^2), 143.8 (d, $^3J_{CP}$ 7 Hz, C^6), 132.9 (d, $^4J_{CP}$ 1.7 Hz, C^p), 131.6 (2C, d, $^2J_{CP}$ 10 Hz, C^o), 128.7 (2C, d, $^3J_{CP}$ 13 Hz, C^m), 128.5 (d, $^1J_{CP}$ 123 Hz, C^i), 117.2 (d, $^2J_{CP}$ 12 Hz, C^3), 114.5 (d, $^4J_{CP}$ 1.7 Hz, C^5); $\boldsymbol{\delta_P}$ (CD_3OD) 12.8; *m/z* (HRMS$^+$) 236.0483 $[M + H]^+$ ($C_{12}H_{10}{}^2H_3NO_3P$ requires 236.0477).

***2*-Bromo-4-[(tert-butoxycarbonyl)amino]pyridine**



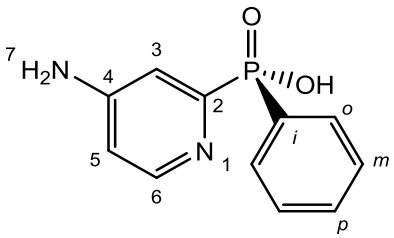
A solution of 4-amino-2-bromopyridine (0.5 g, 2.89 mmol), di-*tert*-butyl dicarbonate (0.99 g, 4.34 mmol) and triethylamine (0.49 mL, 3.47 mmol) in anhydrous CH_2Cl_2 (5 mL) was stirred at 50 °C for 16 h under argon. The solvent was removed under reduced pressure to give a colourless solid that was purified by column chromatography on silica (CH_2Cl_2 : 0.1-1.3% MeOH) to give the title compound as a colourless solid (0.66 g, 84%): $\boldsymbol{\delta_H}$ (400 MHz, $CDCl_3$) 8.22 (1H, d, $^3J_{HH}$ 5.7 Hz, H^6), 7.20 (1H, dd, $^3J_{HH}$ 5.7 Hz $^4J_{HH}$ 2.1 Hz, H^5), 6.95 (1H, d, $^4J_{HH}$ 2.1 Hz, H^3), 6.68 (1H, br s, H^7), 1.56 (9H, s, H^{10}); $\boldsymbol{\delta_C}$ (100 MHz, $CDCl_3$) 150.4 (C^6), 147.2 (C^2), 115.8, 115.6 (C^3, C^5), 111.6 (C^4), 82.4 (C^8), 77.2 (C^9), 28.2 (C^{10}); *m/z* (HRMS$^+$) 273.0239 $[M + H]^+$ ($C_{10}H_{14}BrN_2O_2^+$ requires 273.0173); R_f = 0.40 (silica, CH_2Cl_2: 5% MeOH).

Ethyl phenyl[4-(tert-butoxycarbonyl)aminopyridin-2-yl]phosphinate



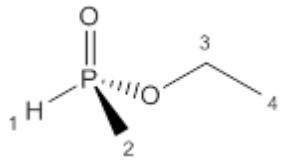
2-Bromo-4-[(tert-butoxycarbonyl)amino]pyridine *(*0.28 g, 1.02 mmol) was added to dry degassed toluene (5 mL). Ethyl phenyl phosphinate (0.18 mL, 1.22 mmol) and triethylamine (0.44 mL, 4.37 mmol) were added and the mixture degassed . [1,1-bis(diphenylphosphino)ferrocene] palladium dichloride (0.058 g, 0.051 mmol) was added and the resulting mixture stirred for 16 h at 120 °C under nitrogen. The solution was diluted with CH_2Cl_2 (5 mL), washed with HCl (2 x 10 mL) and water (3 x 15 mL), dried over K_2CO_3, filtered and the solvent removed under reduced pressure to give a crude residue, that was purified by column chromatography (silica, CH_2Cl_2; MeOH 0-2%) to give the title compound as a yellow oil (0.263 g, 72%): $\boldsymbol{\delta_H}$ (400 MHz, $CDCl_3$) 8.58 (1H, d, $^3J_{HH}$ 5.6 Hz, H^6), 8.11 (1H, dd, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 2.2 Hz, H^3), 7.98 (2H, ddd, *J* 12.2 Hz, *J* 7.9 Hz, *J* 1.6 Hz, H^o), 7.92 (1H, br s, H^7), 7.52 (1H, td, *J* 7.3 Hz, *J* 1.3 Hz, H^p), 7.44 (2H, td, *J* 7.9 Hz, *J* 3.4 Hz, H^m), 4.12 (2H, m, H^{11}), 1.45 (9H, s, H^{10}), 1.36 (3H, t, *J* 6.9 Hz, H^{12}); $\boldsymbol{\delta_C}$ (100 MHz, $CDCl_3$) 152.1 (C^6), 151.7 (d, $^1J_{CP}$ 20 Hz, C^2), 132.4 (d, $^2J_{CP}$ 3 Hz, C^o), 132.2 (d, $^4J_{CP}$ 10 Hz, C^p), 130.4 (C^5) 128.3 (d, $^3J_{CP}$ 13 Hz, C^m), 118.2 (d, $^3J_{CP}$ 25 Hz, C^3), 118.1 (C^8), 113.6 (C^4), 61.6 (C^{11}), 28.1 (C^{10}), 16.5 (C^{12}); $\boldsymbol{\delta_P}$ (162 MHz, $CDCl_3$) 25.9; *m/z* (HRMS$^+$) 363.1474 $[M+H]^+$ ($C_{18}H_{24}N_2O_4P^+$ requires 363.1482); R_f = 0.45 (silica, CH_2Cl_2 : 5% MeOH).

Phenyl(4-aminopyridin-2-yl)phosphinic acid



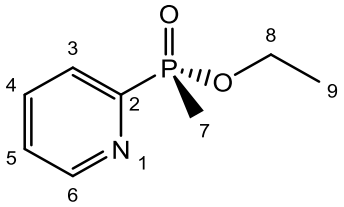
Ethyl phenyl [4-(tert-butoxycarbonyl)aminopyridin-2-yl]phosphinate (0.10 g, 0.33 mmol) was dissolved in HCl (6 M, 4 mL) and the solution stirred at 100 °C for 16 h. The solvent was removed under vacuum at 50 ℃. The residue was washed with methanol (2 × 5 mL) and dried under high vacuum to give the title compound as a colourless solid (quantitative): $\boldsymbol{\delta_H}$ (400 MHz, MeOD) 8.05 (1H, d, $^3J_{HH}$ 5.7 Hz, H^6), 7.92 (2H, dd, $^3J_{HH}$ 7.5 Hz $^4J_{HH}$ 3.0 Hz, H^o), 7.66 (1H, t, $^3J_{HH}$ 7.5 Hz, H^p), 7.57 (2H, td, $^3J_{HH}$ 7.5 Hz $^4J_{HH}$ 3.0 Hz, H^m), 7.25 (1H, dd, *J* 9.7 Hz, *J* 1.9 Hz, H^3), 6.89 (1H, d, $^3J_{HH}$ 5.7 Hz, H^5); $\boldsymbol{\delta_C}$ (100 MHz, MeOD) 160.4 (C^6), 140.9 (C^2), 133.3 (d, *J* 8 Hz, C^o), 131.6 (d, *J* 12 Hz, C^p), 129.0 (d, *J* 14 Hz, C^m), 114.8 (C^i), 113.3 (C^4), 109.4 (C^3, C^5); $\boldsymbol{\delta_P}$ (162 MHz, MeOD) 14.9.

Ethyl methylphosphinate



Diethyl methylphosphonite (0.50 g, 3.67 mmol) was stirred at 0 °C and water was added (63.8 µL, 3.67 mmol). The mixture was allowed to reach 22 °C in 1 hour and then stirred for a further 16 hours under argon. The reaction mixture, containing 1:1 mixture of the title compound and ethanol, was used without further purification (quantitative): $\boldsymbol{\delta_H}$ ($CDCl_3$) 7.20 (1H, d, $^1J_{HP}$ 537 Hz, H^1), 4.15 (1H, ddq, $^2J_{HH}$ -16.7 Hz $^3J_{HP}$ 9.5 Hz, $^3J_{HH}$ 7.1 Hz, H^3), 4.06 (1H, ddq, $^2J_{HH}$ -16.7 Hz $^3J_{HH}$ 9.5 Hz, $^3J_{HH}$ 7.1 Hz, $H^{3'}$), 1.52 (3H, dd, $^2J_{HP}$ 14.0 Hz, $^3J_{HH}$ 4.0 Hz, H^2), 1.35 (3H, t, $^3J_{HH}$ 7.1 Hz $^3J_{HH}$ H^4); $\boldsymbol{\delta_C}$ ($CDCl_3$) 62.3 (d, $^2J_{CP}$ 6.0 Hz, C^3), 16.2 (d, $^3J_{CP}$ 6.0 Hz, C^4), 15.1 (d, $^1J_{CP}$ 94.5 Hz, C^2); $\boldsymbol{\delta_P}$ ($CDCl_3$) 33.4; *m/z* ($HRMS^+$) 109.0418 $[M + H]^+$ ($C_3H_{10}O_2P$ requires 109.0405).

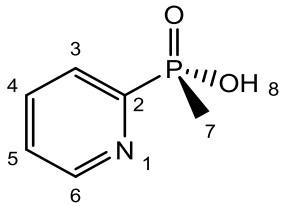
Ethyl methyl(2-pyridyl)phosphinate



2-Bromopyridine (0.60 mL, 6.33 mmol), ethyl methylphosphinate (0.43 g, 4.00 mmol) and triethylamine (0.84 mL, 6.00 mmol) were added to anhydrous degassed toluene (3 mL). [1,1'-Bis(diphenylphosphino)-ferrocene] dichloropalladium(II) (0.029 g, 0.040 mmol) was added and the mixture was degassed by bubbling argon through the stirred solution for 1 h, then heated to reflux

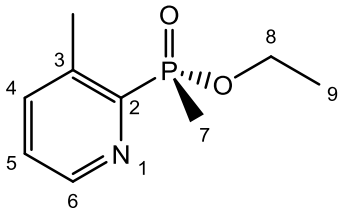
and stirred for 16 h under nitrogen. The solution was diluted with CH_2Cl_2 (20 mL), washed with HCl (1 M, 2 x 25 mL) and water (3 x 20 mL), dried over K_2CO_3, filtered and the solvent removed under reduced pressure to give a yellow oil. Purification by column chromatography on silica (CH_2Cl_2 : 1% MeOH) gave the title compound as a brown oil (0.29 g, 70%): δ_H (400 MHz; MeOD) 8.81 (1H, d, $^3J_{HH}$ 5.0 Hz, H^6), 8.07-7.99 (1H, m, H^5), 8.07-7.99 (1H, m, H^3), 7.62 (1H, td, $^3J_{HH}$ 5.0 Hz $^4J_{HP}$ 2.5 Hz, H^4), 4.01 (2H, q, $^3J_{HH}$ 7.0 Hz, H^8), 1.81 (3H, d, $^2J_{HP}$ 15.0 Hz, H^7), 1.29 (3H, t, $^3J_{HH}$ 7.0 Hz, H^9); δ_C (176 MHz; MeOD) 150.3 (d, $^1J_{CP}$ 20.5 Hz, C^2), 136.7 (d, $^3J_{CP}$ 9.6 Hz, C^6), 127.3 (d, $^2J_{CP}$ 21.6 Hz, C^3), 126.5 (d, $^4J_{CP}$ 3.7 Hz, C^5), 61.4 (d, $^3J_{CP}$ 6.6 Hz, C^4), 15.2 (d, $^2J_{CP}$ 6.2 Hz, C^8), 11.8 (d, $^1J_{CP}$ 103.9 Hz, C^7), 8.0 (d, $^3J_{CP}$ 5.1 Hz, C^9); δ_P (162 MHz; MeOD) 41.8; m/z (ESI+) 186.0680 $[M + H]^+$ ($C_8H_{13}NO_2P$ requires 186.0684); Rf = 0.21 (silica, CH_2Cl_2 : 5% MeOH).

Methyl(2-pyridyl)phosphinic acid



Ethyl methyl(2-pyridyl)phosphinate (0.40 g, 0.22 mmol)) was dissolved in HCl (6 M, 1 mL) and stirred at 100 °C for 16 h. The solvent was lyophilised under high vacuum to give the title compound as a pale brown solid (quantitative): δ_H (400 MHz; MeOD) 8.95 (1H, d, $^3J_{HH}$ 5.5 Hz, H^6), 8.67 (1H, td, $^3J_{HH}$ 7.5 Hz, ^4J 2.0 Hz, $^5J_{HP}$ 1.5 Hz, H^5), 8.42 (1H, ddt, $^3J_{HP}$ 7.5 Hz $^4J_{HH}$ 2.0 Hz $^4J_{HH}$ 1.4 Hz, H^3), 8.17 (1H, t, $^3J_{HH}$ 7.5 Hz, H^4), 1.82 (3H, d, $^2J_{HP}$ 15.6 Hz, H^7); δ_C (100 MHz; MeOD) 157.2 (d, $^3J_{CP}$ 31.8 Hz, C^6), 153.8 (d, $^1J_{CP}$ 138.6 Hz, C^2), 129.0 (d, $^2J_{CP}$ 75.5 Hz, C^3), 121.6 (d, $^3J_{CP}$ 22.2 Hz, C^4), 115.5 (d, $^4J_{CP}$ 11.7 Hz, C^5), 9.5 (d, $^1J_{CP}$ 340.1 Hz, C^7); δ_P (162 MHz; MeOD) 26.2; m/z (ESI+) 158.0369 $[M + H]^+$ ($C_6H_9NO_2P$ requires 158.0371).

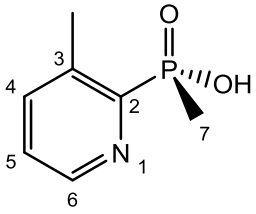
Ethyl methyl(3-methylpyridin-2-yl)phosphinate



A solution of ethyl methylphosphinate (0.48 g, 4.44 mmol), 2-bromo-3-methyl pyridine (49.5 µL, 4.44 mmol), triethylamine (62.0 µL, 4.44 mmol) and toluene (5 mL) was degassed for 2 h by bubbling argon through the solution. [1,1'-Bis(diphenylphosphino) ferrocene]dichloropalladium(II) (0.097 g, 0.13 mmol) was added and the mixture stirred at 120 °C for 16 h under argon. The solvent was removed under reduced pressure and the crude compound purified by column chromatography on silica (CH_2Cl_2 : 2% MeOH) to give the title compound as a dark red oil (0.28 g, 32%). δ_H ($CDCl_3$) 8.52 (1H, d, $^3J_{HH}$ 8.5 Hz, H^6), 7.53 (1H, t, $^2J_{HH}$ 8.5 Hz, H^5), 7.28 (1H, dd, $^3J_{HH}$ 8.5 Hz, $^4J_{HH}$ 4.7 Hz, H^4), 4.11 (1H, dq, $^2J_{HH}$ -16 Hz $^3J_{HH}$ 7.2 Hz, H^8), 4.00 (1H, dq, $^2J_{HH}$ -16 Hz $^3J_{HH}$ 7.2 Hz, $H^{8'}$), 2.69 (3H, s, $H^{3\text{-Me}}$), 1.84

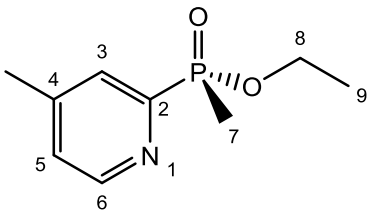
(3H, d, $^{2}J_{HP}$ 15 Hz, H^{7}), 1.30 (3H, t, $^{3}J_{HH}$ 7.2 Hz, H^{9}); **δ_C** ($CDCl_3$) 152.4 (d, $^{1}J_{CP}$ 161 Hz, C^{2}), 146.7 (d, $^{3}J_{CP}$ 21 Hz, C^{6}), 138.8 (d, $^{4}J_{CP}$ 9.5 Hz, C^{5}), 138.5 (d, $^{2}J_{CP}$ 22 Hz, C^{3}), 125.4 (d, $^{3}J_{CP}$ 2.6 Hz, C^{4}), 60.7 (d, $^{2}J_{CP}$ 6.2 Hz, C^{8}), 19.0 (s, $C^{3\text{-}Me}$), 16.4 (d, $^{3}J_{CP}$ 6.3 Hz, C^{9}), 14.0 (d, $^{1}J_{CP}$ 103 Hz, C^{7}); **δ_P** ($CDCl_3$) 44.4; *m/z* ($HRMS^{+}$) 200.0840 $[M + H]^{+}$ ($C_9H_{15}NO_2P$ requires 200.0842).

Methyl (3-methylpyridin-2-yl)phosphinic acid



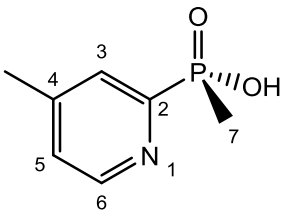
Ethyl methyl (6-methylpyridin-4-yl) phosphinate (0.28 g, 1.4 mmol) was dissolved in a HCl solution (6 M, 1.5 mL) and the mixture was heated at 90 °C for 16 h under argon. The solvent was removed under high vacuum and the brown oil was washed with dry methanol (2 x 2 mL) and dried under high vacuum. The mixture was used without further purification (quantitative): **δ_H** (CD_3OD) 8.76 (1H, d, $^{3}J_{HH}$ 5.6 Hz, H^{6}), 8.57 (1H, dd, $^{3}J_{HH}$ 7.8 Hz $^{4}J_{HH}$ 3.1 Hz, H^{4}), 8.12 (1H, t, $^{3}J_{HH}$ 7.1 Hz, H^{5}), 2.81 (3H, s, $H^{3\text{-}Me}$), 1.82 (3H, d, $^{2}J_{HP}$ 16 Hz, H^{7}); **δ_C** (CD_3OD) 148.9 (d, $^{3}J_{CP}$ 7.1 Hz, C^{4}), 147.3 (d, $^{1}J_{CP}$ 118 Hz, C^{2}), 142.1 (d, $^{2}J_{CP}$ 11.4 Hz, C^{3}), 140.3 (d, $^{3}J_{CP}$ 6.3 Hz, C^{6}), 128.6 (d, $^{4}J_{CP}$ 1.6 Hz, C^{5}), 17.8 (d, $^{3}J_{CP}$ 1.5 Hz, $C^{3\text{-}Me}$), 14.9 (d, $^{1}J_{CP}$ 106 Hz, C^{7}); **δ_P** (CD_3OD) 26.1; *m/z* ($HRMS^{+}$) 172.0527 $[M + H]^{+}$ ($C_7H_{11}NO_2P$ requires 172.0528).

Ethyl methyl(4-methylpyridin-2-yl)phosphinic acid



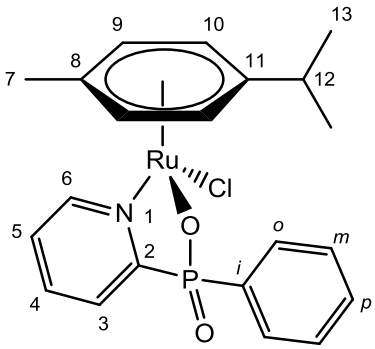
Ethyl methylphosphinate (0.40 g, 3.7 mmol) was dissolved in toluene (5 mL), along with 2-bromo-4-methyl pyridine (0.41 mL, 3.7 mmol) and triethylamine (0.51 mL, 3.7 mmol). Argon was used to degas the solution for 2 h while stirring at room temperature. After the addition of the [1,1'-Bis(diphenylphosphino)ferrocene] dichloropalladium(II) (0.08 g, 0.11 mmol, 3 mol%), the reaction was heated to 120 °C for 16 h. The solvent was removed under reduced pressure and the crude compound dissolved CH_2Cl_2 (20 mL) and washed with water (3 x 20 mL). The organic layer was dried with K_2CO_3, filtered and the solvent removed under reduced pressure. The crude residue was purified by column chromatography on silica (CH_2Cl_2 : 2% MeOH), to give the title compound as a yellow oil (0.38 g, 51%): **δ_H** ($CDCl_3$) 8.64 (1H, d, $^{3}J_{HH}$ 5.0 Hz, H^{6}), 7.94 (1H, d, $^{4}J_{HH}$ 2.2 Hz, H^{3}), 7.25 (1H, dd, $^{3}J_{HH}$ 5.0 Hz $^{4}J_{HH}$ 2.2 Hz, H^{5}), 4.10 (1H, dq, $^{2}J_{HH}$ -10 Hz $^{3}J_{H\text{-}H}$ 8.0 Hz, H^{8}), 3.86 (1H, dq, $^{2}J_{HH}$ -10 Hz $^{3}J_{HH}$ 8.0 Hz, $H^{8'}$), 2.44 (3H, s, $H^{4\text{-}Me}$), 1.78 (3H, d, $^{2}J_{HP}$ 15 Hz, H^{7}), 1.28 (3H, t, $^{3}J_{HH}$ 8.0 Hz, H^{9}); **δ_C** ($CDCl_3$) 154.0 (d, $^{1}J_{CP}$ 156 Hz, C^{2}), 150.2 (d, $^{3}J_{CP}$ 84 Hz, C^{6}), 147.6 (d, $^{2}J_{CP}$ 39 Hz, C^{3}), 127.8 (d, $^{3}J_{CP}$ 86 Hz, C^{4}), 126.6 (d, $^{4}J_{CP}$ 13 Hz, C^{5}), 60.9 (d, $^{2}J_{CP}$ 25 Hz, C^{7}), 21.0 (d, $^{4}J_{CP}$ 5.4 Hz, $C^{4\text{-}Me}$), 16.4 (d, $^{3}J_{CP}$ 25 Hz, C^{8}), 13.5 (d, $^{1}J_{CP}$ 103 Hz, C^{9}); **δ_P** ($CDCl_3$) 40.2; *m/z* ($HRMS^{+}$) 200.0835 $[M + H]^{+}$ ($C_9H_{15}NO_2P$ requires 200.0840).

Methyl(4-methylpyridin-2-yl)phosphinic acid



Ethyl methyl (3-methylpyridin-5-yl)phosphinate (0.38 g, 0.19 mmol), was dissolved in a HCl solution (6 M, 1.5 mL) and the mixture was heated at 90 °C for 16 h under argon. The solvent was removed under high vacuum and the viscous brown oil washed with methanol (3 x 2 mL) and dried under vacuum to give the title compound as a pale brown solid (0.40 g, quantitative): δ_H (CD_3OD) 8.81 (1H, d, $^3J_{HH}$ 6.0 Hz, H^6), 8.33 (1H, d, $^4J_{HH}$ 3.0 Hz, H^3), 8.09 (1H, dd, $^3J_{HH}$ 6.0 Hz $^4J_{HH}$ 3.0 Hz, H^5), 2.77 (3H, s, $H^{4\text{-}Me}$), 1.84 (3H, d $^2J_{HP}$ 16 Hz, H^7); δ_C (CD_3OD) 161.6 (d, $^3J_{CP}$ 32 Hz, C^6), 149.0 (d, $^1J_{CP}$ 124 Hz, C^2), 142.2 (d, $^3J_{CP}$ 29 Hz, C^4), 130.7 (d, $^2J_{CP}$ 46 Hz, C^3), 129.5 (d, $^4J_{CP}$ 4.0 Hz, C^5), 21.1 (s, $C^{4\text{-}Me}$), 14.9 (d, $^1J_{CP}$ 105 Hz, C^7); δ_P (CD_3OD) 26.8; IR (solid) 3358 (O–H), 2916 (C–H), 1448 (P=O), 1620 (P–OH) cm^{-1}; *m/z* ($HRMS^+$) 172.0514 $[M + H]^+$ ($C_7H_{11}NO_2P$ requires 172.0527).

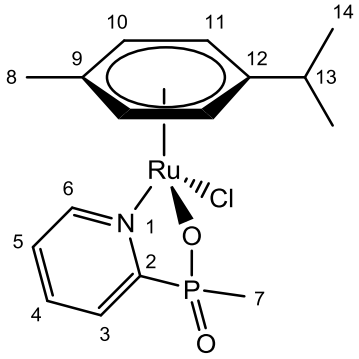
Complex 1



Phenyl(2-pyridyl)phosphinic acid (0.450 g, 1.79 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(*p*-cymene) ruthenium(II) dimer (0.438 g, 0.717 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.368 g, 54%): δ_H (400 MHz CD_3OD) 9.20 (1H, d, $^3J_{HH}$ 4.0 Hz, H^6), 7.93-7.85 (2H, m, H^o), 7.93-7.85 (1H, m, H^4), 7.63 (1H, m, H^5), 7.53-7.49 (1H, m, H^3), 7.42-7.33 (2H, m, H^m), 7.42-7.33 (1H, m, H^p), 5.84 (1H, d, $^3J_{HH}$ 5.7 Hz, H^{10}), 5.79 (1H, d, $^3J_{HH}$ 5.7 Hz, $H^{10'}$) , 5.70 (1H, d, $^3J_{HH}$ 5.7 Hz, H^9), 5.64 (1H, d, $^3J_{HH}$ 5.7 Hz, $H^{9'}$), 2.98 (1H, septet, $^3J_{HH}$ 6.8 Hz, H^{12}), 2.27 (3H, s, H^7), 1.33 (3H, d, $^3J_{HH}$ 6.8 Hz, H^{13}), 1.32 (3H, d, $^3J_{HH}$ 6.8 Hz, $H^{13'}$); δ_C (175 MHz CD_3OD) 160.3 (d, $^1J_{CP}$ 250 Hz, C^2), 155.1 (d, $^3J_{CP}$ 16.7 Hz, C^6), 138.7 (d, $^3J_{CP}$ 15.4, C^4), 133.3 (d, $^1J_{CP}$ 251 Hz, C^i), 133.0 (d, $^2J_{CP}$ 18.3 Hz, C^o), 132.1 (d,

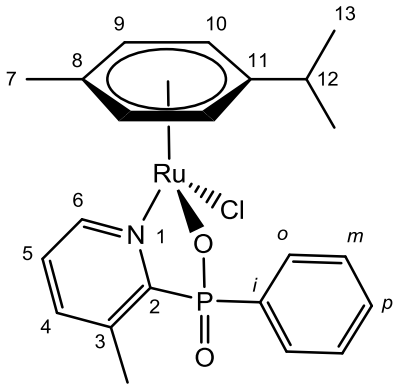
$^{2}J_{CP}$ 4.6 Hz, C^{3}), 128.1 (d, $^{3}J_{CP}$ 23 Hz, C^{m}), 127.9 (d, $^{4}J_{CP}$ 15 Hz, C^{p}) 127.6 (d, $^{4}J_{CP}$ 3.6 Hz, C^{5}), 103.7 (s, C^{11}), 98.0 (s, C^{8}), 81.6 (s, $C^{10'}$), 81.2 (s, C^{10}), 81.1 (s, C^{9}), 81.0 (s, $C^{9'}$), 31.0 (s, C^{12}), 21.6 (s, C^{13}), 21.0 (s, $C^{13'}$), 17.4 (s, C^{7}); $\boldsymbol{\delta_P}$ (162 MHz CD_3OD) 27.6; m/z (ESI+) 448.0613 $[M - Cl]^+$ ($C_{21}H_{23}NO_2P^{96}Ru$ requires 448.0542); Anal. Calcd. for $C_{21}H_{23}ClNO_2PRu.(NaCl)_{0.3}(H_2O)_{0.3}$: C, 49.56; H, 4.67; N, 2.75. Found: C, 49.36; H, 4.66; N, 2.76.

Complex 2



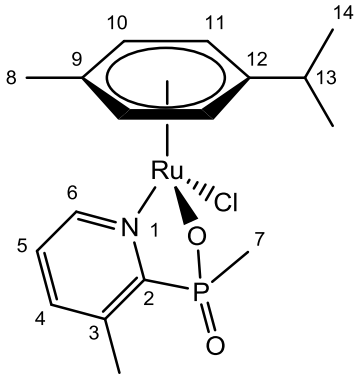
Methyl(2-pyridyl)phosphinic acid (0.400 g, 2.05 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(*p*-cymene)ruthenium(II) dimer (0.40 g, 0.65 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was then dissolved into CH_2Cl_2 (5 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.447 g, 44%). $\boldsymbol{\delta_H}$ (CD_3OD) 9.26 (1H, d, $^{3}J_{HH}$ 6.5 Hz, H^{6}), 8.08 (1H, tdd, $^{3}J_{HH}$ 6.5 Hz $^{4}J_{HP}$ 2.2 Hz $^{4}J_{HH}$ 1.0 Hz, H^{4}), 7.76 (1H, t, $^{3}J_{HH}$ 6.5 Hz, H^{5}), 7.68 (1H, dd, $^{3}J_{HH}$ 6.5 Hz $^{4}J_{HH}$ 2.2 Hz, H^{3}), 5.80 (1H, d, $^{3}J_{HH}$ 6.0 Hz, H^{11}), 5.72 (1H, d, $^{3}J_{HH}$ 6.0 Hz, $H^{11'}$), 5.61 (1H, d, $^{3}J_{HH}$ 6.0 Hz, H^{10}), 5.53 (1H, d, $^{3}J_{HH}$ 6.0 Hz, $H^{10'}$), 2.88 (1H, septet, $^{3}J_{HH}$ 7.0 Hz, H^{13}), 2.21 (3H, s, H^{8}), 1.42 (3H, d, $^{2}J_{HP}$ 15.0 Hz, H^{7}), 1.26 (3H, d, $^{3}J_{HH}$ 7.0 Hz, H^{14}), 1.17 (3H, d, $^{3}J_{HH}$ 7.0 Hz, $H^{14'}$); $\boldsymbol{\delta_C}$ (CD_3OD) 159.3 (d, $^{1}J_{CP}$ 135 Hz, C^{2}), 154.9 (d, $^{3}J_{CP}$ 9.5 Hz, C^{6}), 138.7 (d, $^{2}J_{CP}$ 8.6 Hz, C^{3}), 127.6 (d, $^{4}J_{CP}$ 2.2 Hz, C^{5}), 127.5 (d, $^{3}J_{CP}$ 18.8 Hz, C^{4}), 102.7 (s, C^{9}), 97.9 (s, C^{12}), 81.6 (s, $C^{11'}$), 81.3 (s, C^{11}), 80.8 (s, C^{10}), 80.1 (s, $C^{10'}$), 30.7 (s, C^{13}), 17.7 (d, $^{1}J_{CP}$ 103 Hz, C^{7}), 17.1 (s, C^{8}), 14.0 (s, C^{14}); $\boldsymbol{\delta_P}$ (CD_3OD) 51.1; m/z (ESI+) 386.0379 $[M - Cl]^+$ ($C_{16}H_{21}NO_2P^{96}Ru$ requires 386.0386). Anal. Calcd. for $C_{16}H_{21}ClNO_2PRu.(NaCl)_{1.2}(H_2O)_{0.8}$: C, 38.48; H, 4.56; N, 2.80. Found: C, 38.65; H, 4.50; N, 3.37.

Complex 3



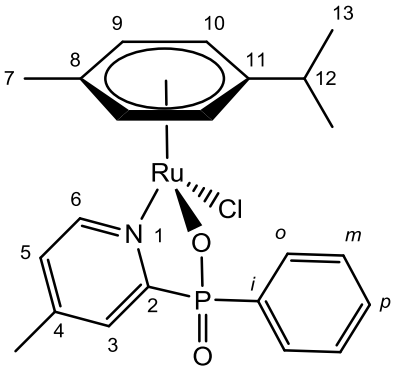
Phenyl(3-methylpyridin-5-yl)phosphinic acid (0.15 g, 0.64 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(*p*-cymene)ruthenium(II)dimer (0.20 g, 0.32 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was then dissolved into CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.17 g, 52%): $\boldsymbol{\delta_H}$ (CD_3OD) 9.08 (1H, d, $^3J_{HH}$ 6.7 Hz, H^6), 7.77 (2H, dd, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 2.0 Hz, H^o), 7.70 (1H, dd, $^3J_{HH}$ 6.7 Hz $^4J_{HH}$ 2.7 Hz, H^4), 7.53 (1H, td, $^3J_{HH}$ 6.7 Hz $^4J_{HH}$ 2.7 Hz, H^5), 7.46 (1H, tt, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 2.0 Hz, H^p), 7.34 (2H, td, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 2.0 Hz, H^m), 5.76 (1H, d, $^3J_{HH}$ 5.9 Hz, H^{10}), 5.72 (1H, d, $^3J_{HH}$ 5.9 Hz, $H^{10'}$), 5.60 (1H, d, $^3J_{HH}$ 5.9 Hz, H^9), 5.58 (1H, d, $^3J_{HH}$ 5.9 Hz, $H^{9'}$), 2.94 (1H, septet, $^3J_{HH}$ 6.9 Hz, H^{12}), 2.21 (3H, s, H^7), 2.04 (3H, s, $H^{3\text{-Me}}$), 1.30 (3H, d, $^3J_{HH}$ 6.9 Hz, H^{13}), 1.28 (3H, d, $^3J_{HH}$ 6.9 Hz, $H^{13'}$); $\boldsymbol{\delta_C}$ (CD_3OD) 157.4 (d, $^1J_{CP}$ 143 Hz, C^2), 152.9 (d, $^3J_{CP}$ 10 Hz, C^6), 140.6 (d, $^3J_{CP}$ 7.7 Hz, C^4), 138.5 (d, $^2J_{CP}$ 18.9 Hz, C^3), 134.0 (d, $^1J_{CP}$ 143 Hz, C^i), 132.8 (d, $^2J_{CP}$ 11 Hz, C^o), 131.6 (d, $^4J_{CP}$ 2.8 Hz, C^p), 127.6 (d, $^3J_{CP}$ 13 Hz, C^m), 127.2 (d, $^4J_{CP}$ 2.1 Hz, C^5), 103.5 (s, C^{11}), 97.7 (s, C^8), 81.4 (s, C^{10}), 81.0 (s, C^9), 30.8 (s, C^{12}), 21.4 (s, C^{13}), 20.7 (s, $C^{13'}$), 17.2 (d, $^3J_{CP}$ 1.9 Hz, $C^{3\text{-Me}}$), 17.1 (s, C^7); $\boldsymbol{\delta_P}$ (CD_3OD) 38.2; *m/z* (HRMS$^+$) 462.0699 $[M - Cl]^+$ ($C_{22}H_{25}NO_2P^{96}Ru$ requires 462.0702); Anal. Calcd. for $C_{22}H_{25}ClNO_2PRu.(NaCl)_{0.3}(H_2O)_{0.3}$: C, 50.54; H, 4.94; N, 2.68. Found: C, 50.65; H, 5.02; N, 2.66.

Complex 4



Methyl (3-methylpyridin-2-yl) phosphinic acid (0.10 g, 0.58 mmol) was dissolved in MeOH (4 mL) and the pH was raised to approximately pH 8 with addition of sodium methoxide methanolic solution. Dichloro(*p*-cymene) ruthenium(II) dimer (0.18 g, 0.29 mmol) was added to the solution and the reaction mixture was stirred for 16 h under argon at room temperature. Methanol was then removed under reduced pressure and the dark red residue dissolved in dichloromethane (3 mL. Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually. A yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid. (0.14 g, 54%): $\boldsymbol{\delta_H}$ (CD_3OD) 9.18 (1H, d, $^3J_{HH}$ 6.4 Hz, H^6), 7.90 (1H, dd, $^3J_{HH}$ 6.4 Hz $^4J_{HH}$ 2.7 Hz, H^4), 7.58 (1H, t, $^3J_{HH}$ 6.4 Hz, H^5), 5.77 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{11}), 5.72 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{11'}$), 5.59 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{10}), 5.52 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{10'}$), 2.90 (1H, septet, $^3J_{HH}$ 7.0 Hz, H^{13}), 2.58 (3H, s, $H^{3\text{-}Me}$), 2.23 (3H, s, H^8), 1.45 (3H, d, $^2J_{HP}$ 15 Hz, H^7), 1.29 (3H, d, $^3J_{HH}$ 7.0 Hz, H^{14}), 1.26 (3H, d, $^3J_{HH}$ 7.0 Hz, $H^{14'}$); *m/z* (HRMS$^+$) 400.0543 [M - Cl]$^+$ ($C_{17}H_{23}NO_2P^{96}Ru$ requires 400.0542).

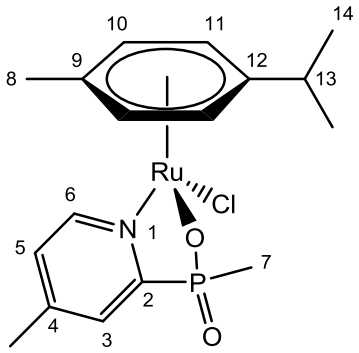
Complex 5



Phenyl(4-methylpyridin-2-yl)phosphinic acid (0.08 g, 0.35 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(*p*-cymene) ruthenium(II) dimer (0.110 g, 0.17 mmol) was added and the suspension was stirred for 16 h under argon at room temperature. The solvent was removed under reduced pressure and the dark red residue dissolved in

dichloromethane (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.14 g, 86%): $\boldsymbol{\delta_H}$ (CD_3OD) 8.98 (1H, d, $^3J_{HH}$ 5.8 Hz, H^6), 7.84 (2H, qdd, $^3J_{HH}$ 14 Hz $^4J_{HP}$ 7.0 Hz $^4J_{HH}$ 1.3 Hz, H^o), 7.48 (1H, td, $^3J_{HH}$ 10 Hz $^4J_{HH}$ 1.3 Hz, H^p), 7.44 (1H, d, $^3J_{HH}$ 5.8 Hz, H^5), 7.36 (2H, td, $^3J_{HH}$ 7.9 Hz $^4J_{HP}$ 3.4 Hz, H^m), 7.15 (1H, dd, $^4J_{HH}$ 7.0 Hz $^5J_{HH}$ 1.9 Hz, H^3), 5.76 (2H, d, $^3J_{HH}$ 7.0 Hz, H^9), 5.62 (2H, d, $^3J_{HH}$ 7.0 Hz, H^{10}), 2.95 (1H, septet, $^3J_{HH}$ 6.8 Hz, H^{12}), 2.35 (3H, s, H^7), 2.24 (3H, s, $H^{4\text{-Me}}$), 1.29 (6H, d, $^3J_{HH}$ 6.8 Hz, H^{13}); $\boldsymbol{\delta_C}$ (CD_3OD) 161.6 (s, C^2), 154.1 (s, C^6), 151.6 (s, C^4), 132.8 (2C, d, $^2J_{CP}$ 10 Hz, C^o), 128.5 (s, C^p), 128.2 (s, C^i), 128.1 (s, C^3), 127.8 (s, C^5), 127.7 (d, $^3J_{CP}$ 14 Hz, C^m), 103.4 (s, C^{11}), 97.7 (s, C^8), 81.26 (s, C^{10}), 80.9 (s, $C^{10'}$), 80.8 (s, C^9), 80.7 (s, $C^{9'}$), 30.8 (s, C^{12}), 19.38 (s, $C^{4\text{-Me}}$), 17.2 (s, C^7), 21.4 (s, C^{13}), 20.8 (s, $C^{13'}$); $\boldsymbol{\delta_P}$ (CD_3OD) 39.0; IR (solid) 3053 (C–H), 1201 (P=O) cm^{-1}; *m/z* ($HRMS^+$) 498.0479 $[M + H]^+$ ($C_{22}H_{26}NO_2ClP^{96}Ru$ requires 498.0466); Anal. Calcd. for $C_{22}H_{25}ClNO_2PRu.(NaCl)_{0.4}(H_2O)_{0.4}$: C, 49.90; H, 4.91; N, 2.64. Found: C, 49.99; H, 4.90; N, 2.67.

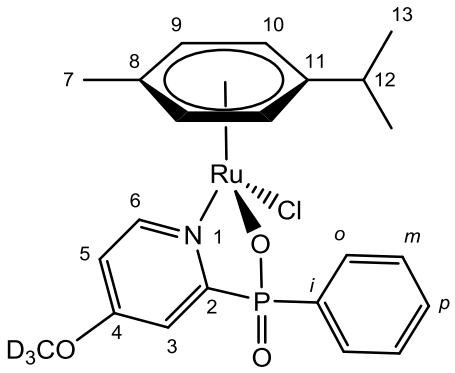
Complex 6



Methyl (4-methylpyridin-2-yl)phosphinic acid (0.13 g, 0.78 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(*p*-cymene) ruthenium(II) (0.24 g, 0.39 mmol) was added and the reaction mixture was heated at 40 °C, stirring under argon for 16 h. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a bright yellow solid (0.16 g, 45%): $\boldsymbol{\delta_H}$ (CD_3OD) 9.07 (1H, d, $^3J_{HH}$ 6.0 Hz, H^6), 7.59 (1H, d, $^4J_{HH}$ 4.0 Hz, H^3), 7.51 (1H, dd, $^3J_{HH}$ 6.0 Hz, $^4J_{HH}$ 4.0 Hz, H^5), 5.77 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{11}), 5.70 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{11'}$), 5.59 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{10}), 5.50 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{10'}$), 2.86 (septet, $^3J_{HH}$ 7.0 Hz, H^{13}), 2.49 (3H, s, $H^{4\text{-Me}}$), 2.19 (3H, s, H^8), 1.40 (3H, d, $^2J_{HP}$ 15 Hz, H^7), 1.25 (3H, d, $^3J_{HH}$ 7.0 Hz, H^{14}), 1.24 (3H, d, $^3J_{HH}$ 7.0 Hz, $H^{14'}$); $\boldsymbol{\delta_C}$ (CD_3OD) 158.5 (d, $^1J_{CP}$ 136 Hz, C^2), 154.1 (d, $^3J_{CP}$ 10 Hz, C^6), 151.6 (d, $^3J_{CP}$ 8.5 Hz, C^4), 128.4 (d, $^4J_{CP}$ 2.0 Hz, C^5), 128.3 (d, $^2J_{C\text{-}P}$ 19 Hz, C^3), 102.5 (s, C^{12}), 97.8 (s, C^9), 81.6 (s, C^{11}), 81.3 (s, $C^{11'}$), 80.8 (s, C^{10}), 79.9 (s, $C^{10'}$), 30.7 (s, C^{13}), 21.3 (s, C^{14}), 20.9 (s, $C^{14'}$), 19.6 (s, $C^{4\text{-Me}}$), 17.8 (d, $^1J_{CP}$ 102

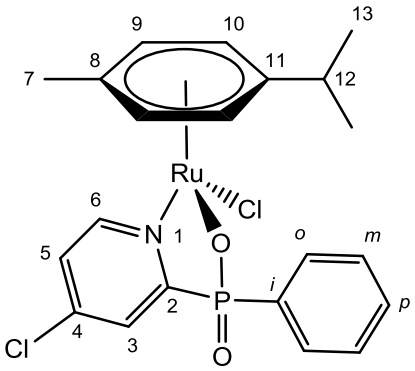
Hz, C^7), 17.2 (s, C^8); δ_P (CD_3OD) 51.2; IR (solid) 2967 (C–H), 1200 (P=O) cm^{-1}; *m/z* ($HRMS^+$) 400.0541 $[M - Cl]^+$ ($C_{17}H_{23}NO_2P^{96}Ru$ requires 400.0542).

Complex 7



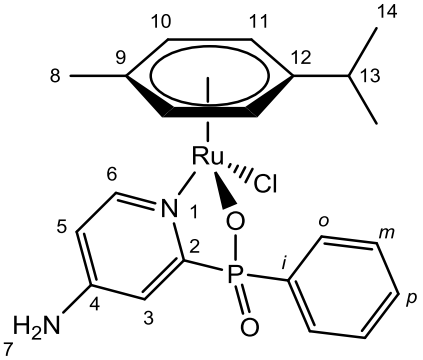
Phenyl (4-3d-methoxypyridin-2-yl)phosphinic acid (0.13 g, 0.53 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~ pH 8 with addition of NaOMe. Dichloro(*p*-cymene)ruthenium(II)dimer (0.16 g, 0.26 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a pale yellow solid (0.050 g, 17%): δ_H (CD_3OD) 8.93 (1H, d, $^3J_{HH}$ 6.7 Hz, H^6), 7.84 (2H, dd, $^3J_{HH}$ 7.2 Hz, H^o), 7.47 (1H, t, $^3J_{HH}$ 7.2 Hz, H^p), 7.36 (2H, td, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 3.0 Hz, H^m), 7.16 (1H, dd, $^3J_{HH}$ 6.7 Hz $^4J_{HH}$ 2.6 Hz, H^3), 6.76 (1H, dd, $^3J_{HH}$ 6.7 Hz $^4J_{HH}$ 2.6 Hz, H^5), 5.75 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{10}), 5.73 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{10'}$), 5.64 (1H, d, $^3J_{HH}$ 6.0 Hz, H^9), 5.57 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{9'}$), 2.95 (1H, septet, $^3J_{HH}$ 6.9 Hz, H^{12}), 2.27 (3H, s, H^7), 1.30 (6H, d, $^3J_{HH}$ 6.9 Hz, H^{13}); δ_C (CD_3OD) 167.3 (d, $^3J_{CP}$ 12 Hz, C^4), 161.0 (d, $^1J_{CP}$ 143 Hz, C^2), 155.7 (d, $^3J_{CP}$ 12 Hz, C^6), 134.5 (d, $^1J_{CP}$ 144 Hz, C^i), 132.7 (2C, d, $^2J_{CP}$ 11 Hz, C^o), 131.9 (d, $^4J_{CP}$ 2.7 Hz, C^p), 127.8 (2C, d, $^3J_{CP}$ 13 Hz, C^m), 114.1 (d, $^4J_{CP}$ 21 Hz, C^5), 113.1 (d, $^2J_{CP}$ 1.6 Hz, C^3), 103.1 (s, C^8), 97.5 (s, C^{11}), 81.0 (s, C^{10}), 80.8 (s, $C^{10'}$), 80.7 (s, C^9), 80.5 (s, $C^{9'}$), 30.8 (s, C^{12}), 21.4 (s, C^{13}), 20.8 (s, $C^{13'}$), 17.3 (s, C^7); δ_P (CD_3OD) 39.2; *m/z* ($HRMS^+$) 481.0842 $[M - Cl]^+$ ($C_{22}H_{22}{}^2H_3NO_3P^{96}Ru$ requires 481.0836).

Complex 8



Phenyl(4-fluoropyridin-2-yl)phosphinate, **L1**, (.050 g, 0.189 mmol) was dissolved in HCl (6M, 2 mL) and the solution was stirred at 30 °C for 16 h. The solvent was removed under reduced pressure and the residue dissolved in methanol (2 × 2 mL) and dried under high vacuum. Hydrolysis and halide exchange were confirmed by mass spectrometry and ^{1}H-NMR. The residue was dissolved in MeOH (2 mL) and the pH adjusted to ~ pH 8 with addition of NaOMe. Dichloro(*p*-cymene)ruthenium(II) dimer (0.040 g, 0.066 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was then dissolved into CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.030 g, 43%): $\boldsymbol{\delta_H}$ (CD_3OD) 9.13 (1H, d, $^{3}J_{HH}$ 7.2 Hz, H^{6}), 7.87 (2H, dd, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HH}$ 1.2 Hz H^{o}), 7.72 (1H, d, $^{4}J_{HH}$ 2.6 Hz, H^{3}), 7.53 (1H, td, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HH}$ 1.2 Hz, H^{p}), 7.42 (2H, td, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 3.0 Hz, H^{m}), 7.33 (1H, dd, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HH}$ 2.6 Hz, H^{5}), 5.86 (1H, d, $^{3}J_{HH}$ 6.0 Hz, H^{10}), 5.81 (1H, d, $^{3}J_{HH}$ 6.0 Hz, $H^{10'}$), 5.72 (1H, d, $^{3}J_{HH}$ 6.0 Hz, H^{9}), 5.66 (1H, d, $^{3}J_{HH}$ 6.0 Hz, $H^{9'}$), 2.99 (1H, septet, $^{3}J_{HH}$ 7.2 Hz, H^{12}), 2.28 (3H, s, H^{7}), 1.34 (6H, d, $^{3}J_{HH}$ 7.2 Hz, H^{13}); $\boldsymbol{\delta_P}$ (CD_3OD) 37.8; *m/z* ($HRMS^{+}$) 482.0156 $[M - Cl]^{+}$ ($C_{21}H_{22}ClNO_2P^{96}Ru$ requires 482.0153).

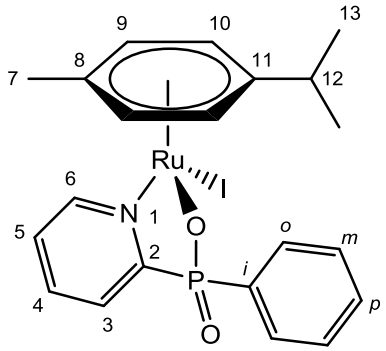
Complex 9



Phenyl(4-aminopyridin-2-yl)phosphinic acid (0.070 g, 0.33 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(*p*-cymene)ruthenium(II)dimer (0.10 g, 0.17 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The

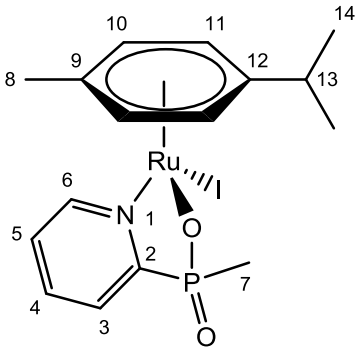
solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess ligand and salts were removed by trituration with cold MeOH (2 × 2 mL) and cold water (2 × 2 mL) to give the title compound as a yellow solid (0.088 g, 53%): **δ_H** (600 MHz, DMSO) 8.39 (1H, d, $^3J_{HH}$ 6.4 Hz, H^6), 7.71 (2H, ddd, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 7.0 Hz $^5J_{HH}$ 1.2 Hz, H^o), 7.37 (1H, td, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 1.2 Hz, H^p), 7.28 (2H, td, $^3J_{HH}$ 7.4 Hz $^4J_{HH}$ 2.7 Hz, H^m), 6.53 (1H, dd, $^3J_{HH}$ 6.4 Hz $^4J_{HH}$ 2.5 Hz, H^5), 6.24 (1H, dd, $^4J_{HH}$ 7.0 Hz, $^5J_{HH}$ 2.4 Hz, H^3), 5.68 (1H, d, $^3J_{HH}$ 5.9 Hz, H^{11}), 5.60 (1H, d, $^3J_{HH}$ 5.9 Hz, $H^{11'}$), 5.57 (1H, d, $^3J_{HH}$ 5.9 Hz, $H^{10'}$) 5.42 (1H, d, $^3J_{HH}$ 5.9 Hz, H^{10}), 2.80 (1H, septet, *J* 5.9 Hz, H^{13}), 2.24 (3H, s, H^8), 1.20 (6H, d, *J* 6.9 Hz, H^{14}); **δ_C** (151 MHz, DMSO) 155.7 (d, $^3J_{CP}$ 5 Hz, C^6), 153.8 (d, $^1J_{CP}$ 6 Hz, C^2), 135.8 (d, $^3J_{CP}$ 6 Hz, C^4), 133.2 (d, $^2J_{CP}$ 8 Hz, C^o), 131.2 (d, *J* 11 Hz, C^p), 127.9 (d, *J* 13 Hz, C^m), 126.8 (C^3), 111.2 (C^i), 101.9 (C^{12}), 96.8 (d, $^3J_{CP}$ 4 Hz, C^9), 80.8 (d, $^3J_{CP}$ 4 Hz, C^{10}), 80.1 (d, $^3J_{CP}$ 4 Hz, C^{11}), 31.1 (d, $^4J_{CP}$ 5 Hz, C^{13}), 22.4 (d, $^4J_{CP}$ 3 Hz, C^8), 18.5 (d, $^5J_{CP}$ 7 Hz, C^{14}); **δ_P** (243 MHz, DMSO) 35.6; *m/z* (HRMS$^+$) 505.0388 $[M + H]^+$ ($C_{21}H_{25}ClN_2O_2PRu^+$ requires 506.0318).

Complex 10



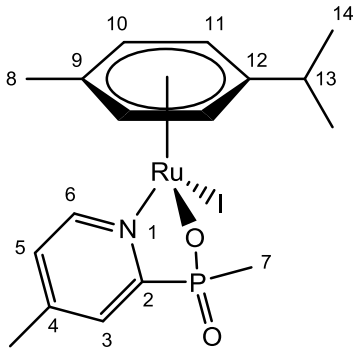
Phenyl(2-pyridyl)phosphinic acid (0.89 g, 4.09 mmol) was dissolved in MeOH (5 mL) and the pH adjusted to ~ pH 8 with addition of NaOMe. Diiodo(*p*-cymene)ruthenium(II) dimer (0.20 g, 0.20 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a pale brown solid (0.060 g, 49%): **δ_H** (700 MHz; MeOD) 9.10 (1H, d, $^3J_{HH}$ 6.5, H^6), 7.92-7.89 (2H, dd, $^3J_{HH}$ 7.0 Hz $^4J_{HH}$ 1.5 Hz, H^o), 7.84 (1H, tdd, $^3J_{HH}$ 6.5 Hz $^4J_{HP}$ 3.2 Hz $^4J_{HH}$ 1.3 Hz, H^4), 7.53 (1H, ttd, $^3J_{HH}$ 6.5 Hz $^4J_{HH}$ 1.5 Hz, H^5), 7.50 (1H, td, $^3J_{HH}$ 6.5 Hz $^4J_{HH}$ 1.5 Hz, H^3), 7.38 (2H, td, $^3J_{HH}$ 7.0 Hz $^4J_{HH}$ 1.5 Hz, H^m), 7.26 (1H, t, $^3J_{HH}$ 7.0 Hz, H^p), 5.77 (2H, 2 doublets, $^3J_{HH}$ 6.1 Hz, H^{10}), 5.66 (2H, 2 doublets, $^3J_{HH}$ 6.1 Hz, H^9), 3.05 (1H, q, $^3J_{HH}$ 7.0 Hz, H^{12}), 2.26 (3H, s, H^7), 1.30 (6H, dd, $^3J_{HH}$ 35.1 $^4J_{HH}$ 6.9 Hz, H^{13}); **δ_C** (176 MHz, MeOD) 160.5 (d, $^1J_{CP}$ 144.6 Hz, C^2), 156.8 (d, $^3J_{CP}$ 10.0 Hz, C^6), 138.1 (d, $^3J_{CP}$ 8.9 Hz, C^4), 133.0 (d, $^1J_{CP}$ 144.5 Hz, C^i), 132.8 (d, $^2J_{CP}$ 10.5 Hz, C^o), 132.0 (d, $^2J_{CP}$ 2.8 Hz, C^3), 127.8 (d, $^3J_{CP}$ 13.3 Hz, C^m), 127.3 (d, $^4J_{CP}$ 20.0 Hz, C^p), 126.87 (d, $^4J_{CP}$ 2.3 Hz, C^5), 104.90 (C^{11}), 97.40 (C^8), 82.1 (d, $^3J_{CP}$ 32.0 Hz, C^9), 80.7 (d, $^3J_{CP}$ 89.9 Hz, C^{10}), 31.5 (d, $^4J_{CP}$ 57.7 Hz, C^{12}), 21.3 (d, $^4J_{CP}$ 79.0 Hz, C^7), 18.0 (C^{13}); **δ_P** (162 MHz, MeOD) 37.6; m/z (ESI+) 575.9670 [M + H]+ ($C_{21}H_{24}INO_2PRu$ requires 575.9665).

Complex 11



Methyl(2-pyridyl)phosphinic acid (0.055 g, 0.35 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Diiodo(*p*-cymene) ruthenium(II) dimer (0.18 g, 0.18 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved into CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a deep red solid (0.059 g, 62%). $\boldsymbol{\delta_H}$ (700 MHz; MeOD) 9.14 (1H, d, $^3J_{HH}$ 5.5 Hz, H^6), 8.03 (1H, dt, $^3J_{HH}$ 5.5 Hz $^4J_{HP}$ 1.5 Hz, H^4), 7.73 (1H, d, $^3J_{HP}$ 5.5 Hz, H^3), 7.63 (1H, td, $^3J_{HH}$ 5.5 Hz $^4J_{HP}$ 1.5 Hz, H^5), 5.70 (2H, 2 doublets, $^3J_{HH}$ 23.1 Hz $^4J_{HP}$ 6.0 Hz, H^{10}), 5.58 (2H, 2 doublets, $^3J_{HH}$ 27.8 Hz $^4J_{HP}$ 6.02 Hz, H^{11}), 3.24 (1H, septet, $^3J_{HH}$ 7.0 Hz, H^{13}), 2.28 (2H, s, H^8), 1.42 (3H, dd, $^2J_{HP}$ 124.7 Hz, H^7), 1.36 (1H, d, H^{14}), 1.26 (1H, d, $H^{14'}$); $\boldsymbol{\delta_C}$ (176 MHz; MeOD) 159.6 (d, $^1J_{CP}$ 136 Hz, C^2), 156.6 (d, $^3J_{CP}$ 9.5 Hz, C^6), 152.3 (d, $^3J_{CP}$ 115.5 Hz, C^{12}), 138.5 (d, $^3J_{CP}$ 8.5 Hz, C^4), 131.8 (d, $^3J_{CP}$ 109 Hz, C^9), 127.5 (d, $^4J_{CP}$ 2.2 Hz, C^5), 127.2 (d, $^2J_{CP}$ 19.3 Hz, C^3), 81.8 (d, $^3J_{CP}$ 78.0 Hz, C^9), 80.8 (d, $^3J_{CP}$ 85.9 Hz, C^8), 21.2 (d, $^4J_{CP}$ 35.1 Hz, C^{13}), 18.0 (C^{14}), 16.7 (d, $^4J_{CP}$ 104.1 Hz, C^8), 11.5 (d, $^1J_{CP}$ 525.2 Hz, C^7); $\boldsymbol{\delta_P}$ (162 MHz; MeOD) 50.6; m/z (ESI+) 513.9502 [M + H]+ ($C_{16}H_{22}INO_2PRu$ requires 513.9509).

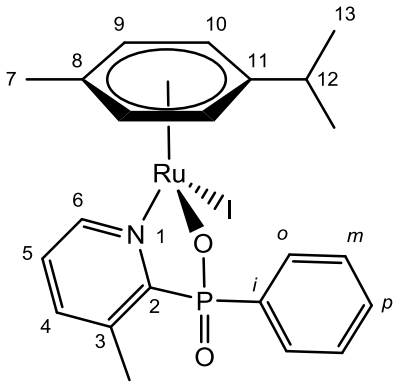
Complex 12



Methyl (4-methylpyridin-2-yl)phosphinic acid (0.040 g, 0.23 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Diiodo(p-cymene) ruthenium(II) dimer (0.10 g, 0.12 mmol) was added and the reaction mixture was stirred at 40 °C under argon for 16 h. The

solvent was removed under reduced pressure to leave a dark orange residue which was then dissolved into CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a dark orange solid (0.082 g, 66%): $\boldsymbol{\delta_H}$ (CD_3OD) 8.96 (1H, d, $^3J_{HH}$ 5.8 Hz, H^6), 7.57 (1H, d, $^3J_{HH}$ 6.2 Hz, H^3), 7.47 (1H, d, $^3J_{HH}$ 5.8 Hz, H^5), 5.70 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{11}), 5.66 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{11'}$), 5.58 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{10}), 5.54 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{10'}$), 2.97 (1H, septet, $^3J_{HH}$ 7.0 Hz, H^{13}), 2.50 (3H, s, $H^{4\text{-Me}}$), 2.28 (3H, s, H^8), 1.41 (3H, d, $^2J_{HP}$ 15 Hz, H^7), 1.28 (3H, d, $^3J_{HH}$ 7.0 Hz, H^{14}), 1.24 (3H, d, $^3J_{HH}$ 7.0 Hz, $H^{14'}$); $\boldsymbol{\delta_C}$ (CD_3OD) 158.7 (1C, d, $^1J_{CP}$ 136 Hz, C^2), 155.8 (1C, $^3J_{CP}$ 10 Hz, C^6), 151.3 (1C, d, $^3J_{CP}$ 8.0 Hz, C^4), 128.3 (1C, d, $^4J_{CP}$ 2.2 Hz, C^5), 127.9 (1C, d, $^2J_{CP}$ 19.0 Hz, C^3), 104.5 (1C, s, C^{12}), 97.0 (1C, s, C^9), 81.9 (1C, s, C^{10}), 81.4 (1C, s, $C^{10'}$), 80.9 (1C, s, C^{11}), 80.5 (1C, s, $C^{11'}$), 31.3 (1C, s, C^{13}), 21.2 (1C, s, $C^{14'}$), 21.1 (1C, s, C^{14}), 19.5 (1C, d, $^4J_{CP}$ 0.7 Hz, $C^{4\text{-Me}}$), 18.3 (1C, s, C^8), 16.7 (1C, d, $^1J_{CP}$ 103 Hz, C^7); $\boldsymbol{\delta_P}$ (CD_3OD) 50.53; *m/z* ($HRMS^+$) 527.9669 $[M + H]^+$ ($C_{17}H_{24}INO_2P^{96}Ru$ requires 527.9665).

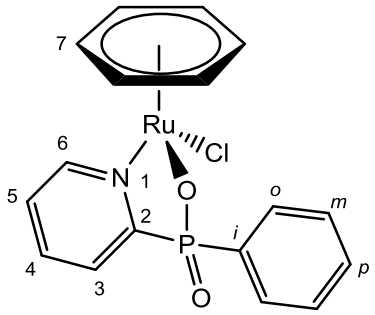
Complex 13



Phenyl(3-methylpyridin-5-yl)phosphinic acid (0.019 g, 0.08 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Diiodo (*p*-cymene) ruthenium (II) dimer (0.04 g, 0.04 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was then dissolved into CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.030 g, 61%): $\boldsymbol{\delta_H}$ (CD_3OD) 9.03 (1H, d, $^3J_{HH}$ 6.5 Hz, H^6), 7.84 (2H, dd, $^3J_{HH}$ 7.0 Hz $^4J_{HH}$ 2.0 Hz, H^o), 7.66 (1H, dd, $^3J_{HH}$ 6.5 Hz, $^3J_{HH}$ 4.0 Hz, H^5), 7.49-7.45 (1H, m, H^4), 7.49-7.45 (1H, m, H^p), 7.34 (2H, td, $^3J_{HH}$ 7.0 Hz $^4J_{HH}$ 2.0 Hz, H^m), 5.66 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{10}), 5.56 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{10'}$), 5.75 (1H, d, $^3J_{HH}$ 6.0 Hz, H^9), 5.70 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{9'}$), 3.02 (1H, septet, $^3J_{HH}$ 7.0 Hz, H^{12}), 2.21 (3H, s, H^7), 2.00 (3H, s, $H^{3\text{-Me}}$), 1.30 (3H, d, $^3J_{HH}$ 7.0 Hz, H^{13}), 1.26 (3H, d, $^3J_{HH}$ 7.0 Hz, $H^{13'}$); $\boldsymbol{\delta_C}$ (CD_3OD) 158.0 (1C, d, $^1J_{CP}$ 144 Hz, C^2), 155.0 (1C, d, $^1J_{CP}$ 10 Hz, C^6), 140.3 (1C, d, $^4J_{CP}$ 8.0 Hz, C^5), 138.1 (1C, d, $^2J_{CP}$ 19 Hz, C^3), 134.0 (1C, d, $^1J_{CP}$ 143 Hz, C^i), 132.7 (2C, d, $^2J_{CP}$ 11.0 Hz, C^o), 131.6 (1C, d, $^4J_{CP}$ 3.0

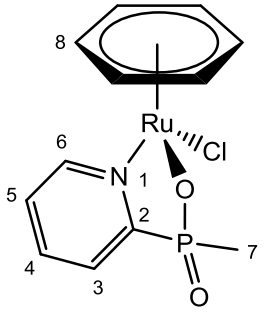
Hz, C^{p}), 127.6 (2C, d, $^{3}J_{CP}$ 13.0 Hz, C^{m}), 104.8 (1C, s, C^{11}), 97.4 (1C, s, C^{8}), 82.2 (1C, s, C^{9}), 82.1 (1C, s, $C^{9'}$), 81.1 (1C, s, $C^{10'}$), 80.7 (1C, s, C^{10}), 31.3 (1C, s, C^{12}), 21.6 (1C, s, C^{13}), 20.9 (1C, s, $C^{13'}$), 17.8 (1C, s, C^{7}), 17.3 (1C, s, $C^{3\text{-Me}}$); $\boldsymbol{\delta_P}$ (CD_3OD) 37.4; *m/z* ($HRMS^{+}$) 589.9827 $[M + H]^{+}$ ($C_{22}H_{26}INO_2P^{96}Ru$ requires 589.9822).

Complex 14



Phenyl(2-pyridyl)phosphinic acid (0.149 g, 0.684 mmol) was dissolved in MeOH (4 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(benzene) ruthenium(II) dimer (0.139 g, 0.228 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a red solid (0.155 g, 78%): $\boldsymbol{\delta_H}$ (400 MHz CD_3OD) 9.27 (1H, d, $^{3}J_{HH}$ 5.6 Hz, H^{6}), 7.95-7.85 (1H, m, H^{4}), 7.86-7.77 (2H, m, H^{o}), 7.60-7.56 (1H, m, H^{5}), 7.55-7.46 (1H, m, H^{3}), 7.43-7.35 (2H, m, H^{m}), 7.33-7.28 (1H, m, H^{p}), 5.97 (6H, s, H^{7}); $\boldsymbol{\delta_C}$ (175 MHz, CD_3OD, partial) 132.9 (d, $^{2}J_{CP}$ 10 Hz, C^{o}), 128.2 (d, $^{3}J_{CP}$ 14 Hz, C^{m}), 127.9 (C^{p}) 127.7 (C^{5}), 83.59 (C^{7}), $\boldsymbol{\delta_P}$ (162 MHz CD_3OD) 39.5; m/z (ESI+) 427.9674 $[M + H]^{+}$ ($C_{17}H_{16}ClNO_2P^{96}Ru$ requires 427.9683).

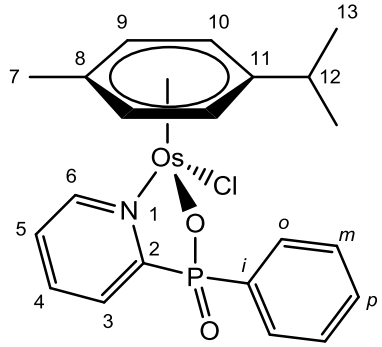
Complex 15



Methyl(2-pyridyl)phosphinic acid (0.110 g, 0.73 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(benzene)ruthenium(II) dimer (0.10 g, 0.20 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was then dissolved into CH_2Cl_2 (5 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL

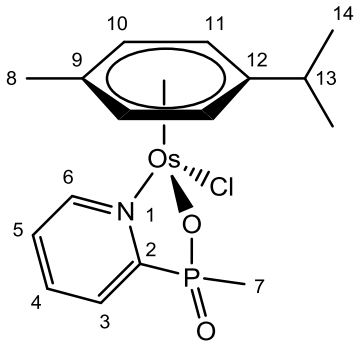
under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 7 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a red solid (0.090 g, 54%): $\boldsymbol{\delta_H}$ (CD_3OD) 9.35 (1H, d, $^3J_{HH}$ 6.0 Hz, H^6), 8.09 (1H, tdd, $^3J_{HH}$ 7.7 Hz $^4J_{HP}$ 3.0 Hz $^4J_{HH}$ 1.0 Hz, H^4), 7.79 (1H, t, $^3J_{HH}$ 6.0 Hz, H^3), 7.71-7.67 (1H, m, H^5), 5.92 (6H, s, H^8), 1.46 (3H, d, $^2J_{HP}$ 15.5 Hz, H^7); $\boldsymbol{\delta_C}$ (CD_3OD) 159.2 (d, $^1J_{CP}$ 140 Hz, C^2), 156.7 (d, $^3J_{CP}$ 9.6 Hz, C^6), 140.4 (d, $^2J_{CP}$ 8.5 Hz, C^3), 129.1 (d, $^4J_{CP}$ 2.2 Hz, C^5), 128.7 (d, $^3J_{CP}$ 19.0 Hz, C^4), 84.6 (s, C^8), 18.6 (d, $^1J_{CP}$ 104 Hz, C^7); $\boldsymbol{\delta_C}$ (CD_3OD) 155.5 (d, $^1J_{CP}$ 130 Hz, C^2), 139.0 (d, $^2J_{CP}$ 8.5 Hz, C^3), 131.2 (d, $^3J_{CP}$ 9.0 Hz, C^6), 127.7 (d, $^4J_{CP}$ 2.0 Hz, C^5), 127.3 (d, $^3J_{CP}$ 19 Hz, C^4), 83.2 (s, C^8), 17.2 (d, $^1J_{CP}$ 103 Hz, C^7); $\boldsymbol{\delta_P}$ (CD_3OD) 51.7; m/z (ESI+) 329.9770 $[M - Cl]^+$ ($C_{12}H_{13}NO_2P^{96}Ru$ requires 329.9760).

Complex 16



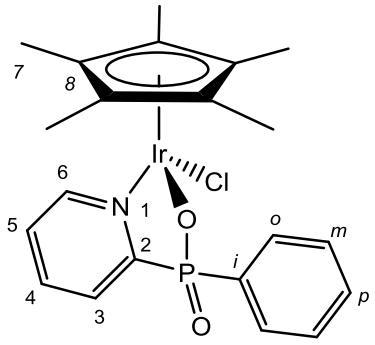
Phenyl(2-pyridyl)phosphinic acid (0.075 g, 0.342 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(*p*-cymene) osmium(II) dimer (0.084 g, 0.106 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a pale brown solid (0.052 g, 42%): $\boldsymbol{\delta_H}$ (400 MHz CD_3OD) 9.08 (1H, d, $^3J_{HH}$ 5.6 Hz, H^6), 8.00 -7.92 (2H, m, H^o), 7.91-7.85 (1H, m, H^4), 7.59-7.50 (3H, m, H^m and H^5), 7.46-7.38 (3H, m, H^p and H^3), 6.22 (1H, d, $^3J_{HH}$ 5.7 Hz, H^{10}), 6.19 (1H, d, $^3J_{HH}$ 5.7 Hz, $H^{10'}$) , 6.07 (1H, d, $^3J_{HH}$ 5.7 Hz, H^9), 6.03 (1H, d, $^3J_{HH}$ 5.7 Hz, $H^{9'}$), 2.82 (1H, septet, $^3J_{HH}$ 7.2 Hz, H^{12}), 2.27 (3H, s, H^7), 1.31 (3H, d, $^3J_{HH}$ 7.2 Hz, H^{13}), 1.27 (3H, d, $^3J_{HH}$ 7.2 Hz, $H^{13'}$); $\boldsymbol{\delta_C}$ (175 MHz, CD_3OD, partial) 133.4 (C^o), 128.5 (C^m), 128.2 (C^p), 100.1 (s, C^{11}), 97.0 (s, C^8), 31.4 (s, C^{12}), 21.3 (s, C^{13}), 21.1 (s, $C^{13'}$), 17.6 (s, C^7); $\boldsymbol{\delta_P}$ (162 MHz CD_3OD) 41.1; m/z (ESI+) 574.0783 $[M + H]^+$ ($C_{21}H_{24}ClNO_2P^{186}Os$ requires 574.0772).

Complex 17



Methyl(2-pyridyl)phosphinic acid (0.058 g, 0.37 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(*p*-cymene)osmium(II) dimer (0.080 g, 0.11 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.042 g, 37%): $\boldsymbol{\delta_H}$ (400 MHz CD_3OD) 9.17 (1H, d, $^3J_{HH}$ 5.7 Hz, H^6), 8.09 (1H, tdd, $^3J_{HH}$ 7.7 Hz $^4J_{HP}$ 3.0 Hz $^4J_{HH}$ 1.4 Hz, H^4), 7.88-7.84 (1H, m, H^3), 7.65-7.61 (1H, m, H^5), 6.20 (1H, d, $^3J_{HH}$ 6.0 Hz, H^{11}), 6.14 (1H, d, $^3J_{HH}$ 6.0 Hz, $H^{11'}$), 5.97-5.94 (2H, m, H^{10}), 2.74 (1H, septet, $^3J_{HH}$ 7.0 Hz, H^{13}), 2.24 (3H, s, H^8), 1.59 (3H, d, $^2J_{HP}$ 15.5 Hz, H^7), 1.26 (3H, d, $^3J_{HH}$ 7.0 Hz, H^{14}), 1.22 (3H, d, $^3J_{HH}$ 7.0 Hz, $H^{14'}$); $\boldsymbol{\delta_P}$ (162 MHz CD_3OD) 54.2; m/z (ESI+) 512.0636 $[M + H]^+$ ($C_{16}H_{22}{}^{35}ClNO_2P^{186}Os$ requires 512.0615).

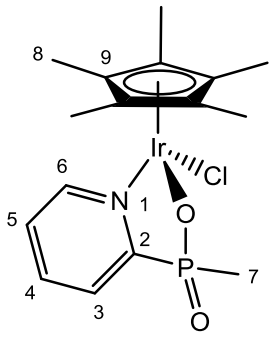
Complex 18



Phenyl(2-pyridyl)phosphinic acid (0.075 g, 0.342 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(pentamethylcyclopentadienyl) iridium(III) dimer (0.050 g, 0.063 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title

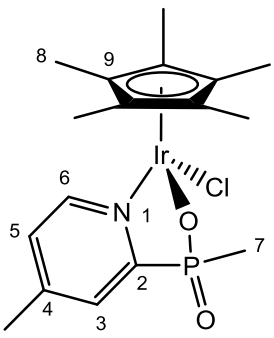
compound as a yellow solid (0.031 g, 42%): **δ_H** (400 MHz CD_3OD) 8.81 (1H, d, $^3J_{HH}$ 5.6 Hz, H^6), 7.99-7.85 (3H, m, H^4 and H^o), 7.66-7.58 (1H, m, H^5), 7.56-7.50 (1H, m, H^3), 7.49-7.35 (3H, m, H^p and H^m), 1.68 (15H, s, H^7); **δ_C** (175 MHz CD_3OD) 159.3 (d, $^1J_{CP}$ 83 Hz, C^2), 149.1 (d, $^3J_{CP}$ 12 Hz, C^6), 137.5 (d, $^3J_{CP}$ 15.4, C^4), 133.4 (d, $^1J_{CP}$ 130 Hz, C^i), 133.1 (d, $^2J_{CP}$ 12 Hz, C^o), 131.6 (d, $^2J_{CP}$ 6 Hz, C^3), 128.3 (d, $^3J_{CP}$ 16 Hz, C^m), 128.2 (d, $^4J_{CP}$ 8 Hz, C^p) 127.6 (d, $^4J_{CP}$ 12 Hz, C^5), 85.1 (s, C^8), 7.8 (s, C^7); **δ_P** (162 MHz CD_3OD) 38.7; m/z (ESI+) 544.1152 $[M - Cl]^+$ ($C_{21}H_{24}NO_2P^{191}Ir$ requires 544.1151).

Complex 19



Methyl(2-pyridyl)phosphinic acid (0.036 g, 0.23 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(pentamethylcyclopentadienyl) iridium(III) dimer (0.050 g, 0.063 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (2 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.046 g, 70%): **δ_H** (CD_3OD) 8.83 (1H, d, $^3J_{HH}$ 5.7 Hz, H^6), 8.11 (1H, tdd, $^3J_{HH}$ 7.7 Hz, $^4J_{HP}$ 3.0 Hz, $^4J_{HH}$ 1.4 Hz, H^4), 7.92-7.88 (1H, m, H^3), 7.72-7.68 (1H, m, H^5), 1.64 (15H, s, H^8), 1.61 (3H, d, $^2J_{HP}$ 15.2 Hz, H^7); **δ_C** (CD_3OD) 161.5 (d, $^1J_{CP}$ 135 Hz, C^2), 154.0 (d, $^3J_{CP}$ 9.1 Hz, C^6), 140.3 (d, $^2J_{CP}$ 8.5 Hz, C^3), 129.8 (d, $^4J_{CP}$ 1.9 Hz, C^5), 129.1 (d, $^3J_{CP}$ 19.0 Hz, C^4), 87.1 (s, C^9), 19.6 (d, $^1J_{CP}$ 105 Hz, C^7), 8.9 (s, C^8); **δ_P** (CD_3OD) 49.8; m/z (ESI+) 482.0982 $[M - Cl]^+$ ($C_{16}H_{22}NO_2P^{191}Ir$ requires 482.0994).

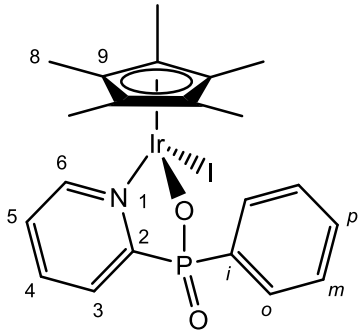
Complex 20



Methyl (4-methylpyridin-2-yl)phosphinic acid (29 mg, 0.17 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Pentamethylcyclopentadienyl iridium dichloride

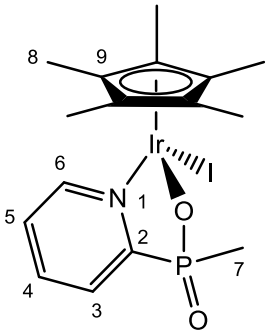
dimer (0.069 g, 0.087 mmol) was added and the solution was stirred at 40 °C for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.047 g, 38%): $\boldsymbol{\delta_H}$ (CD_3OD) 8.61 (1H, d, $^3J_{HH}$ 6.0 Hz, H^6), 7.72 (1H, d, $^4J_{HH}$ 3.5 Hz, H^3), 7.50 (1H, d, $^3J_{HH}$ 6.0 Hz, H^5), 2.52 (3H, s, $H^{4\text{-Me}}$), 1.61 (15H, s, H^8), 1.58 (3H, d, $^2J_{HP}$ 14 Hz, H^7); $\boldsymbol{\delta_C}$ (CD_3OD) 159.3 (d, $^1J_{CP}$ 135 Hz, C^2), 151.8 (d, $^3J_{CP}$ 8.5 Hz, C^6), 151.6 (d, $^2J_{CP}$ 9.5 Hz, C^3), 129.0 (d, $^4J_{CP}$ 2.0 Hz, C^5), 127.9 (d, $^3J_{CP}$ 19 Hz, C^4), 85.5 (5C, s, C^9), 19.6 (d, $^3J_{CP}$ 0.5 Hz, $C^{4\text{-Me}}$), 18.1 (d, $^1J_{CP}$ 104 Hz, C^7), 7.5 (5C, s, C^8); $\boldsymbol{\delta_P}$ (CD_3OD) 50.0; *m/z* ($HRMS^+$) 496.1142 $[M - Cl]^+$ ($C_{17}H_{24}NO_2P^{191}Ir$ requires 496.1151).

Complex 21



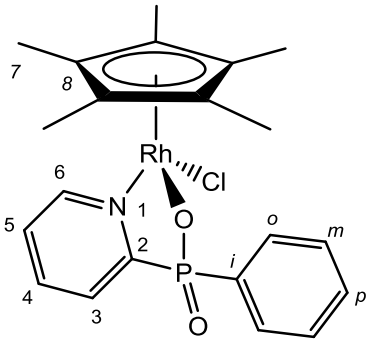
Phenyl(2-pyridyl)phosphinic acid (0.040 g, 0.183 mmol) was dissolved in MeOH (5 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Diiodo(pentamethylcyclopentadienyl) iridium(III) dimer (0.065 g, 0.081 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a pale yellow solid (0.069 g, 87%): $\boldsymbol{\delta_H}$ (700 MHz; MeOD) 8.84 (1H, d, $^3J_{HH}$ 6.0 Hz, H^6), 7.99-7.96 (2H, m, H^o), 7.86 (1H, td, $^3J_{HH}$ 6.0 Hz $^4J_{HP}$ 1.3 Hz, H^4), 7.55–7.49 (1H, m, H^5), 7.55–7.49 (1H, m, H^3), 7.44 (2H, tdd, $^3J_{HH}$ 7.8 Hz $^4J_{HH}$ 2.0 Hz $^5J_{HH}$ 0.4 Hz, H^m), 7.34 (1H, td, $^3J_{HH}$ 7.0 Hz $^4J_{HH}$ 2.0 Hz, H^p), 1.74 (15H, s, H^8); $\boldsymbol{\delta_C}$ (176 MHz; MeOD) 156.5 (d, $^1J_{CP}$ 123.8 Hz, C^2), 139.7 (d, $^3J_{CP}$ 16.5 Hz, C^4), 138.7 (d, $^2J_{CP}$ 135.2 Hz, C^o), 132.9 (d, $^3J_{CP}$ 10.6 Hz, C^6), 131.0 (d, $^3J_{CP}$ 13.6 Hz, C^m), 127.9 (d, $^2J_{CP}$ 28.4 Hz, C^3), 118.0 (d, $^1J_{CP}$ 157.3 Hz, C^i), 86.5 (d, $^3J_{CP}$ 109.2 Hz, C^9), 76.3 (d, $^4J_{CP}$ 25.2 Hz, C^p), 21.0 (d, $^4J_{CP}$ 17.0 Hz, C^8); $\boldsymbol{\delta_P}$ (162 MHz; MeOD) 39.1; m/z (ESI+) 672.0307 $[M + H]^+$ ($C_{21}H_{25}INO_2PIr$ requires 672.0274).

Complex 22



Methyl(2-pyridyl)phosphinic acid (0.039 g, 0.25 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Diiodo(pentamethylcyclopentadienyl) iridium(III) dimer (0.061 g, 0.077 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a yellow precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a yellow solid (0.054 g, 84%): $\boldsymbol{\delta_H}$ (700 MHz; MeOD) 8.82 (1H, d, $^3J_{HH}$ 6.5 Hz, H^6), 8.05 (1H, td, $^3J_{HH}$ 6.5 Hz $^4J_{HH}$ 1.3 Hz, H^4), 7.84 (1H, td, $^3J_{HP}$ 6.0 Hz $^4J_{HH}$ 1.0 Hz, H^3), 7.63 (1H, ddt, $^3J_{HH}$ 5.7 Hz $^4J_{HH}$ 1.5 Hz, H^5), 1.72 (15H, s, H^8), 1.55 (3H, d, $^2J_{HP}$ 15.1 Hz, H^7); $\boldsymbol{\delta_C}$ (176 MHz; MeOD) 154.2 (d, $^3J_{CP}$ 9.0 Hz, C^6), 139.9 (d, $^3J_{CP}$ 32.4 Hz, C^4), 128.2 (d, $^4J_{CP}$ 1.8 Hz, C^5), 127.5 (d, $^2J_{CP}$ 19.0 Hz, C^3), 86.2 (d, $^3J_{CP}$ 134.4 Hz, C^7), 63.7 (d, $^1J_{CP}$ 819.0 Hz, C^2), 18.0 (d, $^1J_{CP}$ 104.8 Hz, C^7), 8.14 (d, $^4J_{CP}$ 126.1 Hz, C^8); $\boldsymbol{\delta_P}$ (162 MHz; MeOD) 49.4; m/z (ESI+) 610.0126 $[M + H]^+$ ($C_{16}H_{23}INO_2PIr$ requires 610.0117).

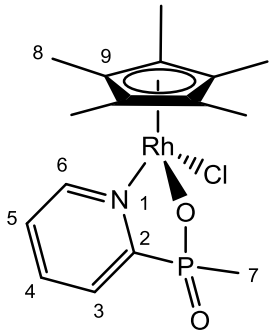
Complex 23



Phenyl(2-pyridyl)phosphinic acid (0.075 g, 0.342 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(pentamethylcyclopentadienyl) rhodium(III) dimer (0.050 g, 0.081 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title

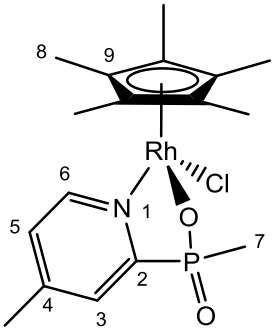
compound as an orange solid (0.054 g, 64%): δ_H (400 MHz CD_3OD) 8.84 (1H, d, $^3J_{HH}$ 5.6 Hz, H^6), 7.99-7.83 (3H, m, H^4 and H^o), 7.72-7.65 (1H, m, H^5), 7.56-7.47 (1H, m, H^3), 7.46-7.32 (3H, m, H^p and H^m), 1.75 (15H, s, H^7); δ_P (162 MHz CD_3OD) 34.3; m/z (ESI+) 457.0677 $[M - Cl]^+$ ($C_{21}H_{25}NO_2P^{103}Rh$ requires 457.0678).

Complex 24



Methyl(2-pyridyl)phosphinic acid (0.046 g, 0.29 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe. Dichloro(pentamethylcyclopentadienyl) rhodium(III) dimer (0.050 g, 0.081 mmol) was added and the reaction stirred at room temperature for 16 h under argon. The solvent was removed under reduced pressure to leave a dark orange residue which was dissolved in CH_2Cl_2 (2 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a deep red solid (0.044 g, 63%): δ_H (CD_3OD) 8.84 (1H, d, $^3J_{HH}$ 5.5 Hz, H^6), 8.10 (1H, tdd, $^3J_{HH}$ 7.7 Hz $^4J_{HP}$ 3.1 Hz, $^4J_{HH}$ 1.4 Hz, H^4), 7.85-7.80 (1H, m, H^3), 7.76-7.72 (1H, m, H^5), 1.69 (15H, s, H^3), 1.48 (3H, d, $^2J_{HP}$ 15.0 Hz, H^7); δ_C (CD_3OD) 162.4 (d, $^1J_{CP}$ 135 Hz, C^2), 153.5 (d, $^3J_{CP}$ 10.0 Hz, C^6), 140.3 (d, $^2J_{CP}$ 9.0 Hz, C^3), 129.3 (d, $^4J_{CP}$ 1.9 Hz, C^5), 128.9 (d, $^3J_{CP}$ 19.7 Hz, C^4), 101.4 (s, C^9), 18.4 (d, $^1J_{CP}$ 104 Hz, C^7), 8.9 (s, C^8); δ_P (CD_3OD) 45.0.

Complex 25



Methyl (4-methylpyridin-2-yl)phosphinic acid (0.039 g, 0.23 mmol) was dissolved in MeOH (2 mL) and the pH adjusted to ~pH 8 with addition of NaOMe (~3 mL) Pentamethylcyclopentadienyl rhodium(III) chloride dimer (0.070 g, 0.11 mmol) was added and the reaction mixture was stirred at 40 °C under argon for 16 h. The solvent was removed under reduced pressure to leave a dark orange

residue which was dissolved in CH_2Cl_2 (3 mL). Excess salts were removed by filtration. The solution volume was reduced to 1 mL under reduced pressure and the concentrated solution was cooled in an acetone : dry ice bath. Diethyl ether (~ 4 mL) was added gradually to the cooled solution and a precipitate formed. The precipitate was filtered using a sintered funnel and dried under high vacuum to give the title compound as a dark orange solid (0.064 g, 63%): $\boldsymbol{\delta_H}$ (CD_3OD) 8.67 (1H, d, $^3J_{HH}$ 5.6 Hz, H^6), 7.68 (1H, d, $^4J_{HH}$ 3.5 Hz, H^3), 7.58 (1H, d, $^3J_{HH}$ 5.6 Hz H^5), 2.52 (3H, s, $H^{4\text{-}Me}$), 1.69 (15H, s, H^8), 1.48 (3H, d, $^2J_{HP}$ 15 Hz, H^7); $\boldsymbol{\delta_C}$ (CD_3OD) 160.2 (d, $^1J_{CP}$ 236 Hz, C^2), 151.6 (d, $^3J_{CP}$ 15 Hz, C^6), 151.2 (d, $^2J_{CP}$ 19 Hz, C^3), 128.7 (d, $^4J_{CP}$ 2.0 Hz, C^5), 128.3 (d, $^3J_{CP}$ 33 Hz, C^4), 94.4 (5C, s, C^9), 19.6 (s, $C^{4\text{-}Me}$), 17.0 (d, $^1J_{CP}$ 179 Hz, C^7), 7.6 (5C, s, C^8); $\boldsymbol{\delta_P}$ (CD_3OD) 45.25; *m/z* ($HRMS^+$) 408.0599 $[M - Cl]^+$ ($C_{17}H_{24}NO_2P^{103}Rh$ requires 408.0600).

3. Biological Assays

(a) Cytotoxicity Measurements

Cytotoxicity of each complex against H460 non-small cell lung carcinoma cells was assessed using the MTT assay[1] as follows: 500 cells were added to 96-flat bottomed well plates and incubated at 37 °C overnight (5% CO_2) in Hanks Balanced Salt Solution (HBSS) (180 µL per well). Assays were also run using 1000 cells per well but results were more consistent when 500 cells per well were used. The tested compounds were dissolved in DMSO and diluted with HBSS media to give 2 mM stock solutions (1% DMSO). The stock solutions were diluted into wells in quadruplicate, to give final concentrations ranging from 0.002 µM to 200 µM (final volume 200 µL, 0.1% final DMSO concentration). The cells were incubated at 37 °C (5% CO_2) for 96 h. After this time, the media was removed and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) solution was added (0.5 mg mL^{-1} in HBSS buffer, 200 µL per well). After 4 h further incubation, the media and MTT were removed and DMSO was added (150 µL). The plate was shaken for 20 seconds and the absorbance of the solutions measured at 550 nm, against controls of (a) pure media (b) media + cells and (c) media + cells + 0.1% DMSO. Using dose response curves, IC_{50} values were determined as the complex concentration required to reduce the absorbance to 50% of that in the untreated, control wells, and represent the mean value for data from at least three independent experiments.

(b) Solubility Assessment

To ensure that the complexes are soluble at the concentrations used for cytotoxicity measurements (200 µM aqueous solution, 0.1% DMSO), complex 1 (1.4 mg, 2.9 µmol) was dissolved in DMSO (14.3 µL). The resulting solution (200 mM, 100% DMSO) was diluted with H_2O (14.3 mL) to give a final concentration of 200 µM in 0.1% DMSO aqueous solution. The solution appears clear to the eye, with no evidence of precipitation. To ensure that this is the case, serial dilutions were made with H_2O (0.1% DMSO) and the absorbance measured at each concentration. The data (Fig S1) obey the Beer Lambert law, confirming that the complexes are fully dissolved at these concentrations. Incidentally, at 270 nm the complex has an extinction coefficient, ε = 6400 mol dm^{-3} cm^{-1}.

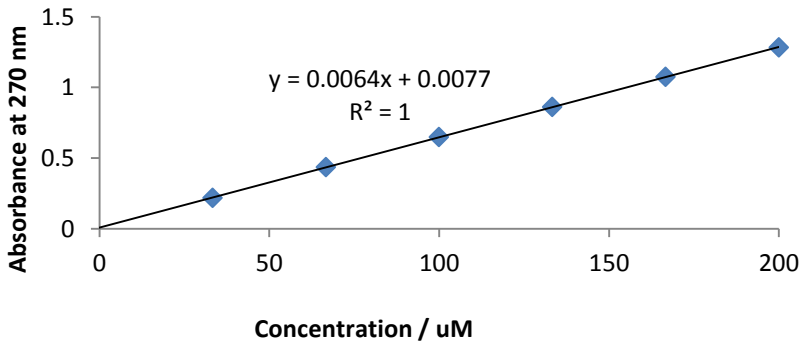


Fig S1. Absorbance at 270nm of complex **1** as a function of concentration (H_2O, 0.1% DMSO, 298 K)

[1] M. V. Berridge, P. M. Herst and A. S. Tan, *Biotechnol. Annu. Rev.*, 2005, **11**, 127.

4. X-Ray Diffraction Procedures

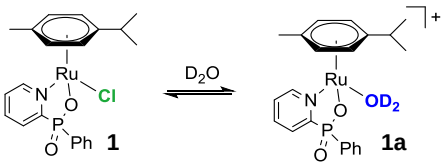
The X-ray single crystal data have been collected using λMoK$_\alpha$ radiation (λ =0.71073Å) on a Bruker D8Venture diffractometer (Photon100 CMOS detector, IμS-microsource, focusing mirrors, 1° ω-scan) equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 120.0(2)K. The structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using SHELXTL [G.M. Sheldrick, *Acta Cryst.* (2008), **A64**, 112-122] and OLEX2 [O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. *Appl. Cryst.* (2009), **42**, 339-341.] software. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were placed in the calculated positions and refined in riding mode. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1457275 and 1457276.

Crystal data for **Complex 3**: $C_{22}H_{25}ClNO_2PRu$ (M = 502.92): monoclinic, space group $P2_1/c$, a = 12.5685(6), b =8.1196(4), c = 20.4312(10) Å, β = 91.535(2)°, V = 2084.3(2)Å^3, Z = 4, T = 120.0(1) K, μ(λMoK$_\alpha$) = 0.975 mm^{-1}, D_{calc} =1.603 g mm^{-3}, 43150 reflections measured, 5811 unique reflections (R_{int} = 0.0528) were used in all calculations. The final R_1 was 0.0309 (4673 > 2σ(I)) and $wR_2$was 0.0629 (all data), GOF = 1.040.

Crystal data for **Complex 20**: $C_{17}H_{24}ClIrNO_2P$ x H_2O (M = 551.01): monoclinic, space group Cc, a = 14.7318(2), b = 16.6565(2), c = 8.3433(1) Å, β = 107.664(2)°, V = 1950.75(4)Å^3, Z = 4, T = 120.0(1) K, μ(λMoK$_\alpha$) = 7.078 mm^{-1}, D_{calc} =1.876 g mm^{-3}, 20026 reflections measured, 5620 unique reflections (R_{int} = 0.0416) were used in all calculations. The final R_1 was 0.0202 (5436 > 2σ(I)) and $wR_2$was 0.0497 (all data), GOF = 1.076, Flack parameter 0.033(5), Hooft parameter 0.042(6).

5. Aqueous Behaviour Procedures and Data

(a) chloride : aqua adduct equilibrium



Complex **1** (5 mg) was dissolved in D_2O:MeOD 9:1 and ^{1}H-NMR spectra (298 K, 400 MHz) were measured over 24 h to investigate position of chloride : aqua adduct equilibrium (Fig S2, (c) - (f)). For reference, the spectra of the chloride (Fig S2 (a)) and aqua (Fig S2 (b)) adducts are also shown. The chloride adduct is retained by dissolving complex **1** in NaCl solution (0.15 M, D_2O:MeOD 9:1). The D_2O adduct is generated by addition of addition of $AgNO_3$ (1.2 equivalents) to **1** (D_2O:MeOD 9:1) with stirring for 10 min, followed by filtration of the AgCl precipitate.

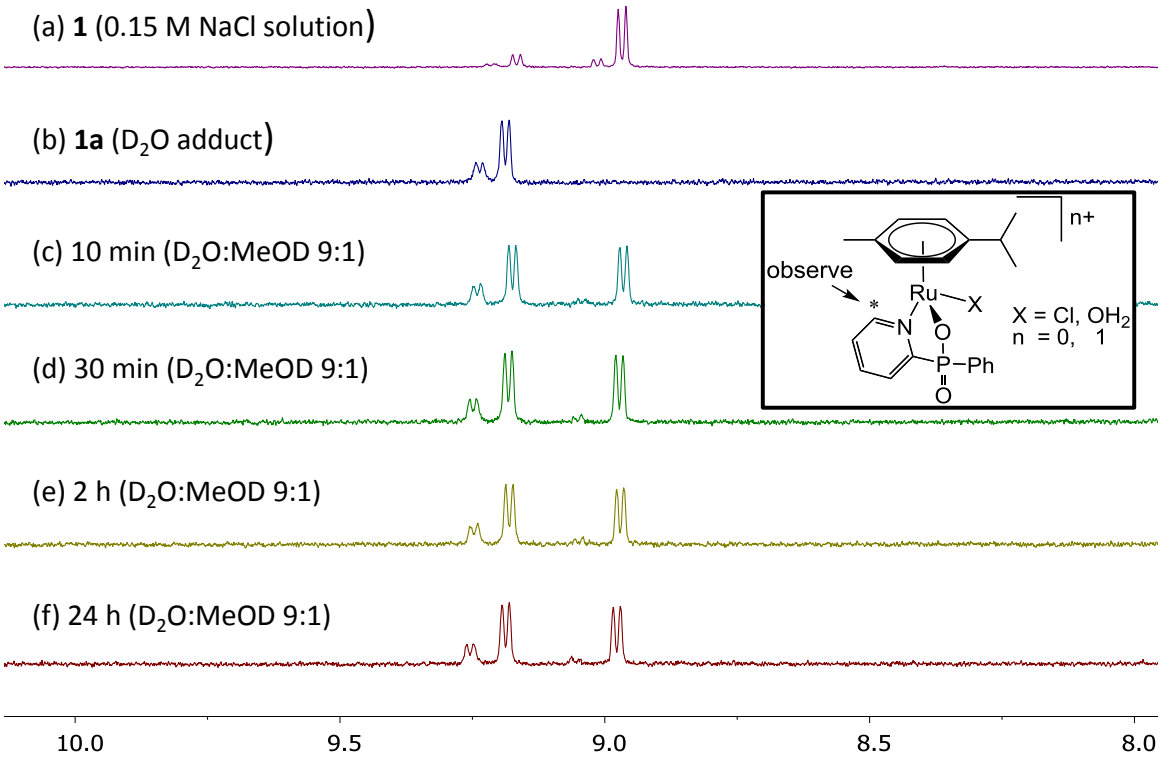


Figure S2. ^{1}H-NMR spectra (298 K, 400 MHz,) of complex **1**: *(c)* to *(f)* in (D_2O:MeOD 9:1) solution over the course of 24 h; *(a)* in 0.15 M NaCl solution (D_2O:MeOD 9:1), leading to the chloride adduct; *(b)* in D_2O:MeOD 9:1, following addition of $AgNO_3$ and filtration of insoluble silver salts, leading to the D_2O adduct (**1a**).

(b) pK_a determination

NMR spectroscopy (^{1}H and ^{31}P) was used to measure the pK_a of selected aqua complexes by measuring the shift of specific peaks at varying pH (Fig S3). In a typical experiment, the selected complex was dissolved in D_2O:MeOD 9:1. Addition of $AgNO_3$, followed by filtration of the AgCl precipitate results in the D_2O adduct. The pH* (pH in D_2O) of solution was varied using NaOD and DNO_3. Triphenylphosphine (-5 ppm) dissolved in $CDCl_3$ contained in a sealed lock tube and dioxane (3.6 ppm) were used as a reference peaks to ensure accurate chemical shift measurement. pK_a* (pK_a measured in D_2O) values were determined from equation S1, using least squares non-linear regression, according to established procedures .[25] pK_a* values were converted to pK_a values using the established equation pK_a = 0.929pK_a* + 0.42.[26] See Fig S4 for pK_a determination of selected aqua complexes.

$$\delta_{obs} = \delta_{H_2O} + \frac{(\delta_{OH} - \delta_{H_2O})}{1+10^{(pH-pKa)}} \qquad \text{Eq S1}$$

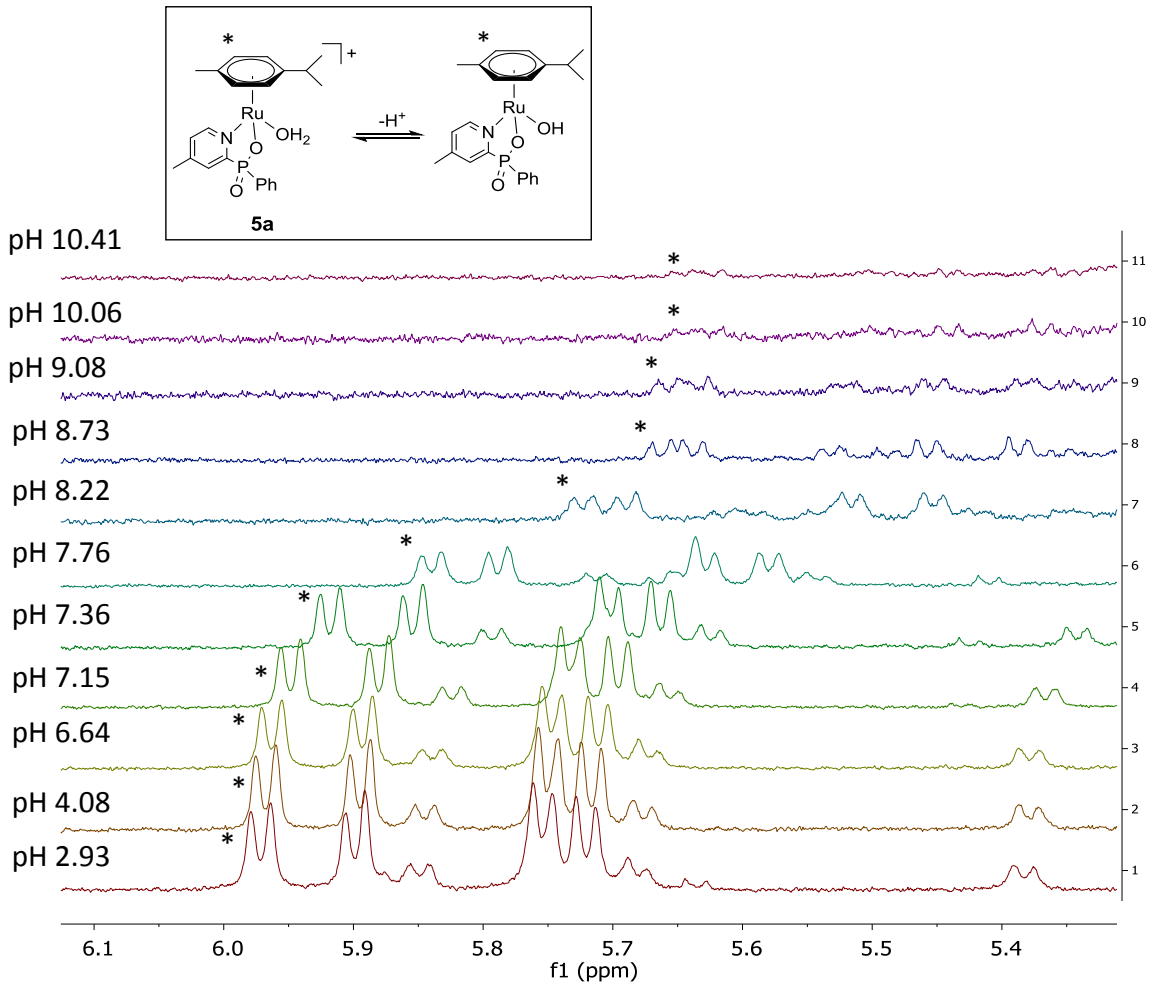
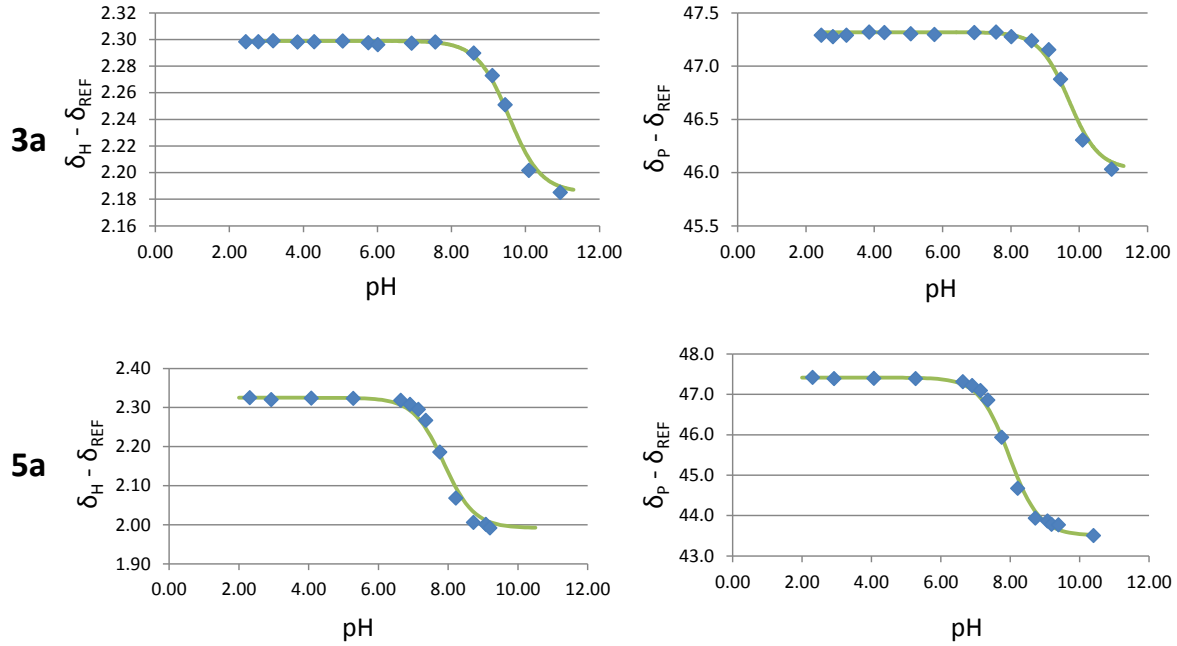


Fig S3. ^{1}H-NMR spectrum (D_2O:MeOD 9:1) of complex **5a** at various pH. Insert shows peaks under observation.



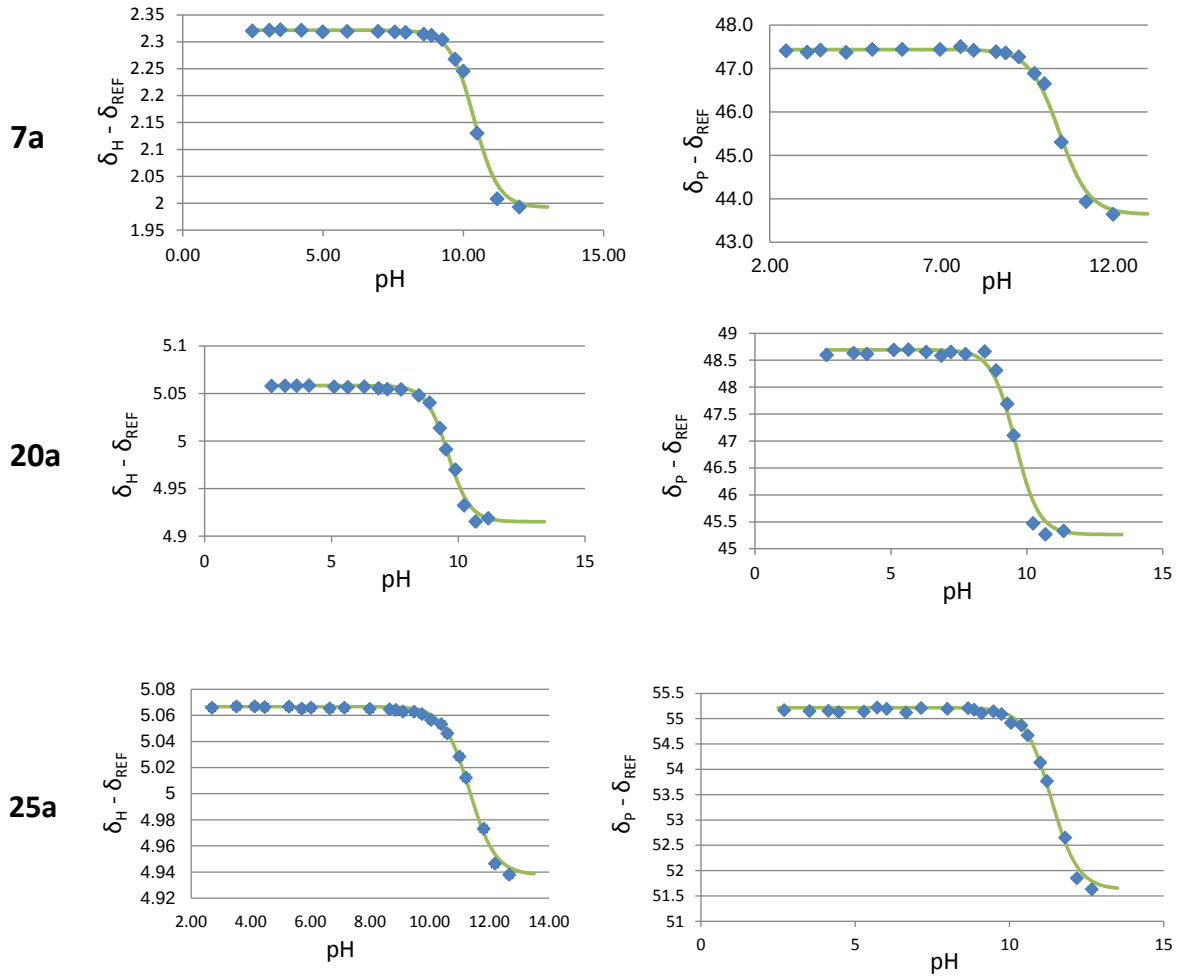


Figure S4. pK_a determination for selected aqua complexes. Left hand column shows ^{1}H-NMR analyses, right-hand column shows ^{31}P-NMR analyses. ^{31}P chemical shifts are reported as observed shift minus shift of reference PPh_3 (in sealed lock tube). ^{1}H chemical shifts are reported as observed shift minus shift of reference dioxane (in sealed lock tube).

(c) Formation of hydroxy-bridged dimer

For each of the studied Ru complexes, the hydroxyl-bridged dimer D1 (Figure S5) forms at strongly basic pH (typically >pH 11), with concomitant loss of the pyridylphosphinate ligand.

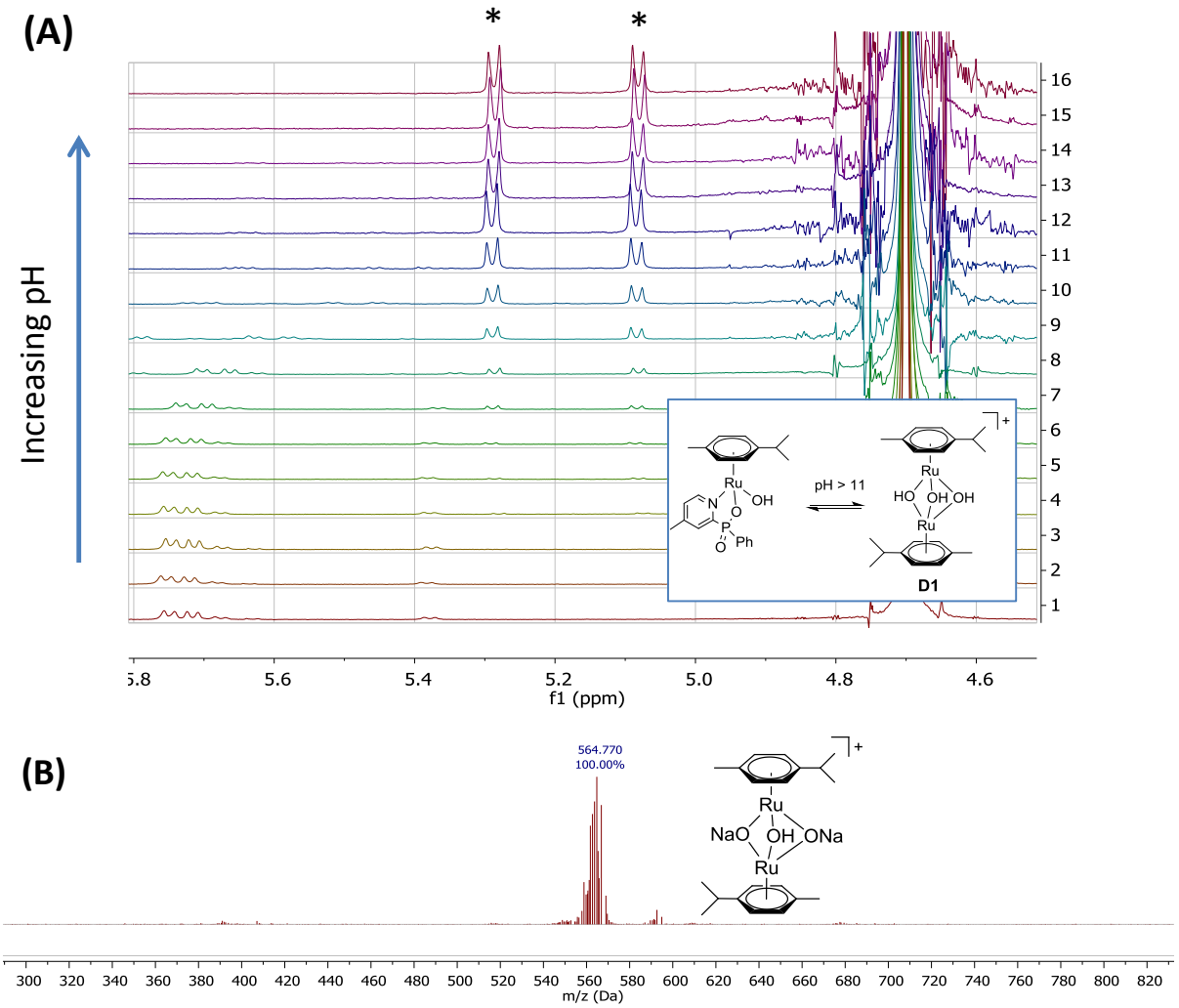


Fig S5. Evidence for the formation of hydroxyl-bridged dimer **D1** from (**A**) ^{1}H-NMR titration (D_2O:MeOD 9:1, 298 K, 400 MHz, pH 7 - 12) – peaks marked with * denote the resonances arising from the aromatic protons in the dimeric species – and (**B**) mass spectrometry.